LIST OF ADVERTISERS.

Members are desired when making enquiries or placing orders with advertisers to mention that they have seen their announcement in the Journal.

W. Christie & Grey, Ltd.
A. F. Craig & Co., Ltd.
Duke & Ockenden, Ltd.
Foster Wheeler, Ltd.
W. J. Fraser & Co., Ltd.
Hadfields, Ltd.
Hayward-Tyler & Co., Ltd.
National Supply Corporation.
John G. Stein & Co., Ltd.
The Tintometer, Ltd.
University of Birmingham.

PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Mr. A. J. Brown has returned from Penang.

Mr. R. K. Dickie is home from Persia.

Mr. C. A. A. T. Dorans has left for Palestine.

Mr. H. D. Fletcher, of Trinidad, is in England until the end of October.

Mr. E. Kodyen has left Greece and is now in Canada.

Mr. J. Macdonald is home from Egypt.

Mr. D. G. Pidgeon has returned from Persia.

Mr. C. S. Snodgrass is in New York, U.S.A.

Mr. P. A. Stiff is home from Persia.

Mr. G. E. Stott has returned from South Africa.

The Secretary would be glad to hear of the whereabouts of the following members:—E. E. G. Agius, J. G. Beastall, T. E. Beaumont, G. Bourkoff, A. F. Brown, A. E. C. Corbet, E. H. Crush, A. Eaton, W. H. Farrand, W. M. Gray, A. L. Greig, T. B. C. Harris, E. J. D. Hewitt, L. B. Holloway, P. N. Hulme, A. MacLean, J. McWilliams, F. A. I. Muntz, F. Naficy, R. E. Palmer, R. K. Van Sickle, and L. N. White.

OBITUARY.

HERBERT BARRINGER.

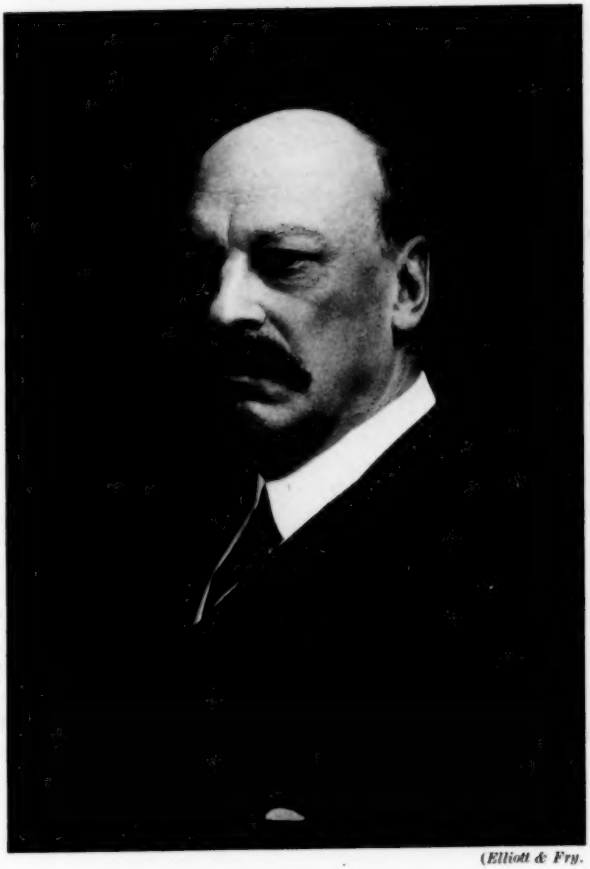
We regret to record the death of Mr. Herbert Barringer, which occurred on August 15.

Born in London in 1856, Mr. Barringer was a pupil with Ravenhill, Hodgson & Co., and later Maudsley, Son & Field. After being with the P. & O. Company for some time he was, at the age of 29, appointed superintendent engineer to Scrutton & Co. In 1887 he founded, with the late Mr. C. M. Jacobs, the business of consulting engineers and naval architects under the title of Jacobs & Barringer. The title of the firm was subsequently changed to Jacobs, Barringer & Garratt, Ltd., and until his retirement in 1931 he was chairman and managing director. The firm developed a large practice in the design and supervision of the construction of oil-tank steamers, and among the companies for whom he acted were C. T. Bowring & Co., the Burmah Oil Co., the Anglo-Persian Oil Co., Lobitos Oilfields, Ltd., Andrew Weir & Co., the Eagle Oil Transport Co., and the Anglo-American Oil Co. Apart from marine installations, he had a great deal to do with the design and construction of oil storages and pipe-lines both at home and abroad. He collaborated with the late Sir Boverton Redwood for many years, and a well-known device with which both their names are associated is the Redwood-Barringer Water Finder.

He was an Original Member of the Institution, and occupied the Presidential Chair during the Sessions, 1923-1924, 1924-1925. He was also a Member of the Institution of Civil Engineers, of the Institution of Mechanical Engineers, of the Institution of Naval Architects, and of the Institute of Marine Engineers.

DINNER CLUB.

The attention of members is drawn to the Dinner Club of the Institution. This Club holds informal dinners after each General Meeting of the Institution and members may invite guests. Those desiring to receive notice of these dinners are requested to inform the Secretary of the Institution.



(*Elliott & Fry.*

HERBERT BARRINGER.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

SPECIAL SUMMER MEETING.

A SPECIAL SUMMER MEETING of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, Adelphi, London, on Tuesday, June 14, 1932.

The following Testing Instruments were demonstrated and described in a series of short lectures :—

Falling Sphere Viscometer.—By A. R. Thomas and D. C. Broome. An instrument of the falling-sphere type for measuring viscosity, in which the passage of the ball through the liquid is detected by an electrical apparatus.

Automatic Electric Penetrometer.—By A. R. Thomas.

The Strobophonometer.—By R. Stansfield. An apparatus used for the analysis of sounds occurring at regular intervals. (See J.I.P.T., 1932, 18, 513–525.)

Testing Lubricating Oil Stock.—By A. A. Ashworth. A method by which lubricating oil stock can be tested to ascertain the yield of oils of specified viscosities.

The Integrating Photometer.—By E. S. L. Beale. An instrument for the measurement of the percentage of light absorbed by the brown film on kerosine lamp chimneys.

The Herschel Oiliness Machine.—By Dr. F. H. Garner. A film illustrating the manufacture and laying of asphalt paving materials was also shown by Highways Construction, Ltd.

An exhibition of apparatus and objects of interest was also arranged as follows :—

The Original Redwood Viscometer.—By the Institution of Petroleum Technologists. The original instrument used by the late Sir Boverton Redwood, Bart., in his work on viscosity.

Measurement of Smoke Point.—By the Institution of Petroleum Technologists. A lamp designed by a Special Sub-Committee of the Standardization Committee for determining the smoke point of kerosine.

Spontaneous Ignition Temperature Apparatus.—By the Royal Aircraft Establishment. The apparatus designed for the determination of S.I.T. and of the delay period. (See J.I.P.T., 1932, 18, 533–547.)

Falling Sphere Viscometer.—By the Royal School of Mines. An instrument for detecting in a simple manner the passage of the ball in a falling-sphere viscometer.

The Testing of Standard Apparatus.—By the National Physical Laboratory. A series of eight photographs illustrating the methods used for testing hydrometers, volumetric glassware and thermometers.

Oil Field Model.—By the Anglo-Persian Oil Co. A working model of a typical limestone field, showing the effect of oil production on gas, oil and water in the limestone reservoir.

Model Refinery.—By the Anglo-Persian Oil Co. A working model showing the flow of the crude oil and the products through a modern refinery.

The Photobitometer.—By the Limmer and Trinidad Lake Asphalt Co. An instrument for the rapid determination of the solid bitumen contact of asphaltic materials.

The other exhibits comprised a working model of a Zublin Rotary Drilling Bit (Mr. M. A. Ockenden); a device for taking horizontal cores (Mr. A. Beeby Thompson); samples of asphalt paving materials (Messrs. Highways Construction, Ltd.); and a display of special or unusual testing apparatus (The Asiatic Petroleum Co. and Shell Marketing, Ltd.) which included the Scott-Snell pump, the Richardson constant level device, the use of headphones on a synchronous timing system for the penetration test, and various types of viscometers, flash-point testers, distillation apparatus, etc.

Improved Methods of Examining Mineral Oils, Especially the High-boiling Components of Non-aromatic Character.*

By J. C. Vlugter, H. I. Waterman and H. A. van Westen.

Introduction.

The usual methods of examining mineral oil fractions still leave much to be desired in many respects. The most important objection is that sulphuric acid is used in order to get an idea of the ratio between paraffins, olefines, aromatics and naphthenes. In order to remove olefines it has been suggested to use diluted sulphuric acid of the most varying concentrations. Whereas opinions differed very much at first in regard to what was the most satisfactory concentration, in the course of time it has become evident that it is impossible to conceive of a concentration with which olefines are completely removed without affecting the aromatics. Further objections to this method are that polymerisation takes place between the olefines one with the other and that condensation reactions occur between olefines and aromatics. Every method of separating olefines and aromatics with the aid of sulphuric acid must be considered to be wrong in principle, since they can only yield approximate results.[1] It goes without saying that a determination of olefines should be based on the unsaturation—that is to say, either the halogen value or the hydrogen value should be determined. Of the methods of determining the halogen value that of McIlhiney is to be preferred. This method enables the substitution to be determined and gives for a number of olefines theoretical results corresponding to the hydrogen absorption during catalytic hydrogenation.[2]

The quantity of halogen (or hydrogen) absorbed is a measure for the number of olefinic double bonds present.

The determination of aromatics with the aid of the drop in the aniline point is impossible if unsaturated hydrocarbons are present, since unsaturated compounds influence the aniline point in an unknown way. These must first be removed in one of the following ways :—

(*a*) By bromination at low temperature and distilling off the unchanged hydrocarbons; the theoretical quantity of bromine is indicated by the bromine value;

* Paper received December 1st, 1931.

[1] D. A. Howes, *J.I.P.T.*, 1930, **16**, 54.

[2] H. I. Waterman, P. van't Spijker, H. A. van Westen, *Rec. Trav. Chim.*, 1929, **48**, 612, 1097, 1103, 1191; H. I. Waterman and H. A. van Westen, *Rec. Trav. Chim.*, 1929, **48**, 637, 1084.

(*b*) By selective hydrogenation at room temperature with the aid of very active catalysts such as palladium, whereby the olefines are converted into paraffins without hydrogenation of the aromatics.[3]

In general, the latter method is to be preferred.

After the determination of the aromatics in the saturated oil has been made with the aid of the drop in the aniline point,[4] the percentage of naphthenes is *estimated* from the absolute value of the aniline point of the aromatic-free oil. The influence of 1 per cent. naphthene on the aniline point of the paraffin is sometimes assumed to be 0·2° C.; the aniline point of the individual naphthenes depends very much on their nature. For instance, 1 per cent. decaline results in a drop in the aniline point of 0·37°.[5] The aromatic determination with concentrated sulphuric acid is more difficult in the case of the higher fractions than it is with the low-boiling fractions. Discolouration and the formation of sulphur dioxide is often observed, which is caused by the complicated nature of the compounds.

The individual hydrocarbons cannot be considered as representatives of one certain type (paraffinous, naphthenic or aromatic), but are always combinations of several types; for instance, aromatics and naphthenes with paraffinous side-chains and compounds which in themselves embody the character of all types. Take, for instance, tetra-hydronaphthaline with an aliphatic side-chain. Such a compound would be *completely* removed with concentrated sulphuric acid, so that the quantity of hydrocarbons removed by shaking with concentrated sulphuric acid gives a wrong idea of the quantity of aromatic *rings*. Moreover, a part of the paraffins and naphthenes is already removed, so that it is impossible to deduce the exact ratio of these from the remaining aromatic-free oil. Considered from this standpoint, observation of the contraction during the sulphuric-acid treatment is to be rejected, whereas the rise of the aniline point may still be serviceable, as this gives a better idea of the quantity of aromatic rings. It would also be advisable in this case to discontinue the treatment with sulphuric acid entirely and to replace this by a complete catalytic hydrogenation of the aromatics in the manner adopted by Willstätter and others. This question will be referred to later.

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[3] Diss. H. A. van Westen, Delft, 1931.

[4] G. Chavanne and L. J. Simon, *Compt. rend.*, 1919, **168**, 111, 1324; Tizard and Marshall, *J.S.C.I.*, 1921, **40**, 20T; H. I. Waterman and J. N. J. Perquin, *Rec. trav. chim.*, 1922, **41**, 192; J. Carpenter, *J.I.P.T.*, 1926, **12**, 518; 1928, **14**, 446; Brame and Hunter, *J.I.P.T.*, 1927, **13**, 794; Sachanen and Wirabianz, *Petrol*, 1929, **25**, 867.

[5] Sachanen and Wirabianz, *loc. cit.*

In order to judge all fractions it is necessary to know the nature of the products in connection with their contents of aromatic rings, naphthenic rings and paraffins, it often being a matter of less importance how the groups of different character are connected one to the other. In this connection the favourable influence of aromatics for obtaining a gasoline (anti-knock gasoline) with a high H.U.C. value should be borne in mind, whereas in kerosine with a slight tendency to soot, aromatic rings are undesirable. Moreover, there is little sense in considering a compound such as cymene $CH_3—C_6H_4—C_3H_7$ to be quantitatively an aromatic without taking into account the aliphatic side-chains.

The factors that are used to calculate a percentage of aromatics or naphthenes from the drop in the aniline point can better be applied to the quantity of aromatic or naphthenic rings. These rings only form a part of the hydrocarbon molecule, but it is only necessary to know this part and not the whole of the said molecule. Neither will it be necessary to know the quantity of sulphur *compounds* in order to determine the sulphur content. Finally it is questionable whether it is necessary to determine the percentage of unsaturated *compounds*, as in this case also it is probable that the total quantity of double bonds present is a measure for judging the unsaturation. This quantity is at once indicated by the bromine value, that is, the percentage by weight of bromine combined additively.

The Principle of the Improved Method.

It has already been stated that attempts have been made to make a distinction between aromatic rings respectively naphthenic rings and side-chains. To this end use has been made of the so-called specific refraction of Lorenz-Lorenz :—

$$\frac{n^2-1}{n^2+2} \cdot \frac{1}{d},$$

in which n represents the index of refraction and d the density at the same temperature. This function was preferred as it is the only exact one, whilst as function of the molecular weight it has advantages above the molecular refraction for the plotting of the graph.

If the specific refraction for paraffins, olefines, naphthenes and aromatics of approximately equal molecular weight is calculated from n_d and d, then the lowest values are found for the naphthenes. In this respect the specific refraction is distinguished from other physical properties such as density, index of refraction and aniline point, which in the case of the types of hydrocarbons mentioned increase or decrease in the order indicated. *The last-mentioned course*

is shown by the specific refractions calculated from the atom refractions,[6] but only in the case of the paraffins and naphthenes do these correspond to the values found experimentally, whilst the values found for aromatics and olefines are considerably higher than those calculated, as a result of the increase in the index of refraction for these two groups.

Some specific refractions determined from the physical constants are given below in comparison with the values calculated from the atom refractions.

	$n\frac{t}{d}$	$d^t/4$	t	$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$	Spec. refr. calculated from the atom refraction.
Paraffins :—					
n-octane	1·3975	0·7030	20°	0·3429	0·3428
n-decane	1·4124	0·7312	20°	0·3405	0·3402
n-hexadecane ..	1·4351	0·7751	20°	0·3367	0·3361
Naphthenes :—					
Cyclo-hexane ..	1·4264	0·7787	20°	0·3293	0·3294
1–1 dimethyl cyclo-hexane	1·4232	0·773	20°	0·3295	0·3294
α-β dicyclo-hexyl-ethane	1·480	0·8838	20°	0·3214	0·3214
Cyclo-pentane ..	1·4086	0·7505	20°	0·3291	0·3294
Cis-decaline ..	1·48035	0·8951	18°	0·3176	0·3183
Aromatics :—					
Benzene	1·5010	0·878	20°	0·3356	0·2706
Diphenyl	1·5882	0·9896	77·1°	0·3402	0·2598
Naphthaline ..	1·582	0·962	98·4°	0·3469	0·2576

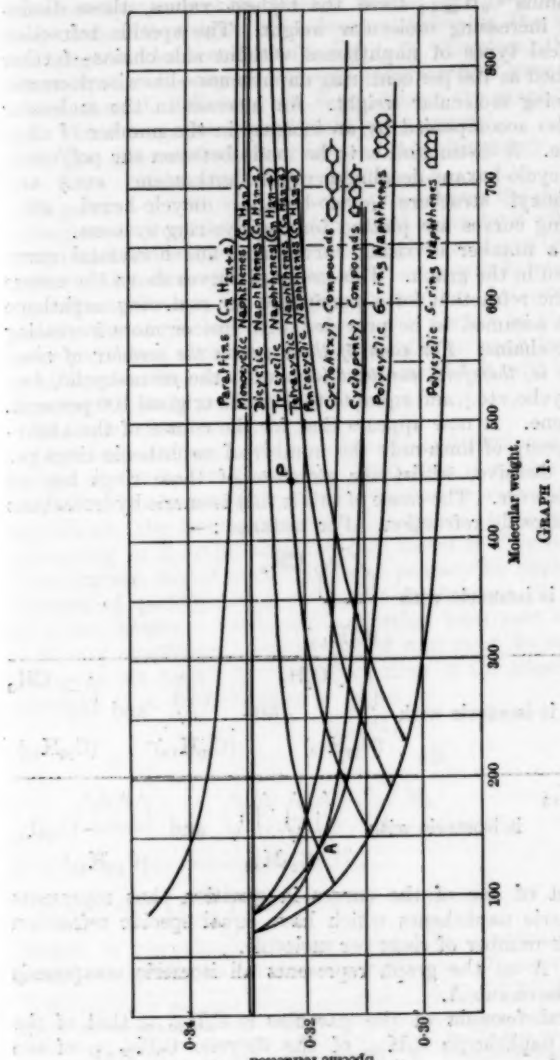
In the case of mixtures of hydrocarbons, it may be expected that the specific refraction is in linear relation to the composition. This was checked with a few mixtures of hydrocarbons of unequal specific refraction and molecular weight.

Decaline	0·3185
Octane	0·3435
Hexadecane	0·3365

	Specific refraction. Calculated.	Found.
50 parts by weight decaline + 50 „ „ octane	0·3310	0·3310
50 „ „ hexadecane + 50 „ „ decaline	0·3275	0·3276

Graph 1 shows the specific refraction as function of the molecular weight; the calculated specific refractions for the paraffins and for a large number of conceivable types of naphthenes are included; points belonging to a certain series are joined by continuous curves, so that each curve represents a certain series.

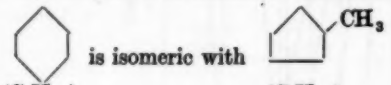
[6] The known Eisenlohr's values have been used.


Paraffins (C_nH_{2n+2})
Monocyclic Naphthenes (C_nH_{2n})
Bicyclic Naphthenes (C_nH_{2n-2})
Tricyclic Naphthenes (C_nH_{2n-4})
Tetracyclic Naphthenes (C_nH_{2n-6})
Pentacyclic Naphthenes (C_nH_{2n-8})
Cyclohexyl Compounds
Cyclopentyl Compounds
Polycyclic 6-rings Naphthenes
Polycyclic 5-rings Naphthenes
P
A
0·34
0·32
0·30
Specific refraction
100
200
300
400
500
600
700
800
Molecular weight.

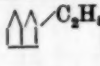
GRAPH 1.

The paraffins C_nH_{2n+2} have the highest values, these diminishing with increasing molecular weight. The specific refraction of the typical types of naphthenes without side-chains—further to be described as 100 per cent. ring naphthenes—likewise decreases with increasing molecular weight. An increase in the molecular weight is also accompanied by an increase in the number of rings per molecule. A distinction is to be made between the polycyclic structure (cyclo-hexane-decaline-perhydro-anthracene, etc.) and the cyclo-hexyl structure (cyclo-hexane, dicyclo-hexyl, etc.). Corresponding curves are plotted for the five-ring systems.

Further, a number of rising curves and one horizontal curve are to be seen in the graph. This group of curves shows the course of the specific refraction for a *purely* 100 *per cent. ring* naphthene when this is assumed to be provided with one or more increasing paraffin side-chains. *For each of these curves the number of rings per molecule is, therefore, constant* (one with the mono-cyclic, two with the dicyclic, etc.), and equal to that of the original 100 per cent. ring naphthene. It now appears that for the course of the above-mentioned group of lines only the number of naphthenic rings per molecule is decisive, whilst the *structure* of these rings has no influence whatever. The cause of this is that isomeric hydrocarbons have equal specific refraction. For instance :—

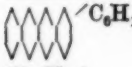


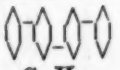
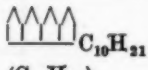
(C_6H_{12}) is isomeric with (C_6H_{12})

A. $(C_{10}H_{18})$ is isomeric with 

$(C_{10}H_{18})$ and $(C_{10}H_{18})$ and

$(C_{10}H_{18})$



$(C_{24}H_{42})$ is isomeric with  $C_{24}H_{42}$ and 

$(C_{24}H_{42})$

Each point of one of the curves in question thus represents *various* isomeric naphthenes which have equal specific refraction and the same number of rings per molecule.

The point A on the graph represents all isomeric compounds mentioned above sub A.

The general formula of the paraffins is C_nH_{2n+2}, that of the mono-cyclic naphthenes C_nH_{2n}, of the dicyclic C_nH_{2n-2}, of the tri-cyclic C_nH_{2n-4}, etc., whilst the number of rings per molecule is nought, one, two, three, etc., respectively. Since the distance

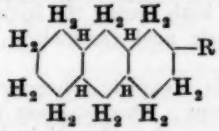
between these curves in relation one to the other is equal with each molecular weight, this distance indicates the influence of one ring on the specific refraction. If, therefore, the index of refraction, the density and the molecular weight have been determined, then the following can be read from the graph :—

1. The average number of rings per molecule[7].
2. The general formula (that is, the elementary composition for a certain molecular weight).

In general, points will be found lying *between* the curves, and in consequence interpolation will be applied, whereby it will be possible to interpolate between one of the higher and one of the lower curves. The choice of the curves between which interpolation is applied is arbitrary ; the result for the number of rings per molecule and for the elementary composition will always be the same. In order to deduce a certain ratio of paraffin to naphthene from the specific refraction and the molecular weight it will be necessary to assume some type of naphthene.

Example of calculation :

Let us assume that a specific refraction of 0·3225 and a molecular weight of 450 is found. In the graph this is represented by the point P. This point is to be understood as representing a tricyclic naphthene, the average number of carbon rings per molecule amounting to 3. This result is also found if P is considered to be a mixture, say of monocyclic and pentacyclic naphthenes, or a mixture of paraffins and polycyclic naphthenes (5 or 6 rings). In order, however, to determine further *what part of the carbon is in ring structure*, a certain type of ring must be assumed, say, polycyclic six rings. If naphthenic rings of the decaline type are assumed, then the following is found :—



R is then approximately $C_{18\cdot4}H_{37\cdot8}$.

In this case $\left(\frac{14}{32\cdot4}\right)100$ = about 43 per cent. of the carbon is present in naphthenic ring structure. It is actually no longer possible to speak of a content of naphthenes. If, nevertheless, it is

[7] Provisionally we shall confine ourselves to the five and six rings, as the knowledge of the other rings, such as three and four rings, apart from whether these occur in large numbers in mineral oils, is really too small to warrant our including them in the investigation. F. Eisenlohr and E. Wöhlisch (*Ber.*, 1920, **53**, 1753) determine the influence of these rings on the molecular, or specific, refraction.

desired to state a "naphthenic" and "paraffin" percentage, then one could interpolate between the line of the paraffins with 0 per cent. carbon in naphthenic rings and that of the polycyclic six-ring naphthenes with 100 per cent. carbon in naphthenic ring structure; a content of 39 per cent. "naphthenes" and 61 per cent. "paraffins" is then found for P. It is preferred, however, to keep to the figures for the average number of carbon rings per molecule and the elementary composition, since both these figures are completely defined. The elementary composition (formula) of the product is $C_nH_{2n-4}O$.

Although this method embodies principles in themselves, already known in its entirety, it is to be considered as new. The question may be asked, however, what is the practical significance of the method suggested. This question is obvious, since mixtures of paraffins and naphthenes do not frequently occur. Formerly this was the case to a still greater degree, but of recent years in consequence of hydrogenation having been introduced into the analysis—to which reference has been made in the introduction—and the development made in hydrogenation technique in the petroleum industry, mixtures of saturated hydrocarbons have become more important.[8] By means of hydrogenation, products can be obtained which are indeed to be considered as mixtures of paraffins and naphthenes, or internal molecular combinations of these groups.

The mixtures of hydrocarbons necessary for this investigation can also be obtained by treating aromatic base materials with sulphuric acid until these are completely freed from aromatic rings. Further, the course of the hydrogenation and the removal of the aromatics can be checked from the specific refraction, since this always diminishes, both during the hydrogenation and in the treatment with sulphuric acid (aromatics have a high specific refraction).

The hydrogenation is complete, therefore, when the specific refraction no longer drops; when shaking with sulphuric acid is continued for a long time, after the original drop there is even a gradual rise in the specific refraction—that is to say a minimum is exceeded. This rise is to be ascribed to the removal of naphthenes during a treatment of long duration. The specific refraction is thus a means of checking refining processes. The above-mentioned drop in the specific refraction was observed in the case of all the natural oils examined, which were of very varied origin; in other words all original oils contain aromatics. These remarks

[8] A summary of the technical position of hydrogenation is found in C. Ellis's "Hydrogenation of Organic Substances," 3rd edition, New York, 1931.

are, of course, only applicable to mixtures of *hydrocarbons*. It is to be expected that very small quantities of sulphur and oxygen compounds will not cause disturbance. These compounds occur in only very small quantities in raffinates and hydrogenation products ; the latter may even be practically free from sulphur.

Aniline Points of Mixtures of Naphthenes and Paraffins.

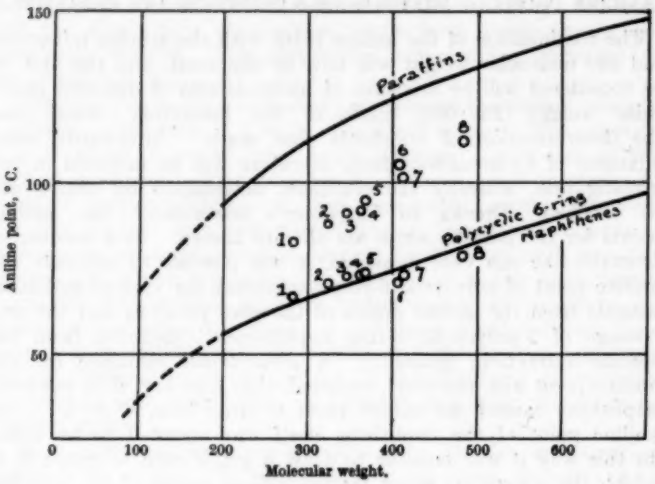
The combination of the aniline point with the specific refraction and the molecular weight will now be discussed, and the first to be considered will be mixtures of hydrocarbons of different molecular weight (250–600) made in the laboratory, where also the determination of constants was made. Afterwards some mixtures of hydrocarbons from literature will be included in the investigation, whereby the constants determined by others will be checked. Thanks to Carpenter's researches,[9] the aniline points for the paraffin series are already known. As a number of aromatic-free oils were available, it was possible to calculate the aniline point of polycyclic 6-ring naphthenes for various molecular weights from the aniline points of the pure paraffins and the percentage of "polycyclic 6-ring naphthenes" (deduced from the specific refraction, graph 1). A *proportional* influence on the aniline point was, therefore, assumed, that is to say, if 50 per cent. naphthene caused the aniline point to drop from a° to a-b°, the aniline point of the naphthene itself was assumed to be a-2b°. In this way it was possible to draw a graph such as graph 2, in which the curves are given for the aniline points of the paraffins and the polycyclic naphthenes for various molecular weights. In this graph horizontal lines connect up equal aniline points of the oils with different naphthenic content and molecular weight.

The connection between graphs 1 and 2 is that it is possible to calculate the percentage of polycyclic 6-ring naphthenes from both—in graph 1 from the specific refraction and in graph 2 from the aniline point. It is possible, therefore, to combine both graphs, and this has been done in graph 3, which, however, only includes the range of molecular weights from 250 to 600. In the case of an aromatic-free oil of which the index of refraction, density and molecular weight are known, it is possible, therefore, from graph 3 to read not only the number of carbon rings per molecule and the elementary composition, but also the aniline point. Inversely, the molecular weight and elementary composition can be read from the specific refraction and the aniline point.

In further explanation it may be mentioned that it is not necessary to assume that it is just polycyclic 6-ring naphthenes that are

[9] *J.I.P.T.*, 1928, **14**, 461.

present. The construction of the aniline point curves in graph 3 is *quite independent* of such an assumption. Graph 2 might be omitted entirely and only serves as explanation. The result is that in the specific refraction molecular weight diagram simply the *points of equal aniline point are connected by curves.*[10]

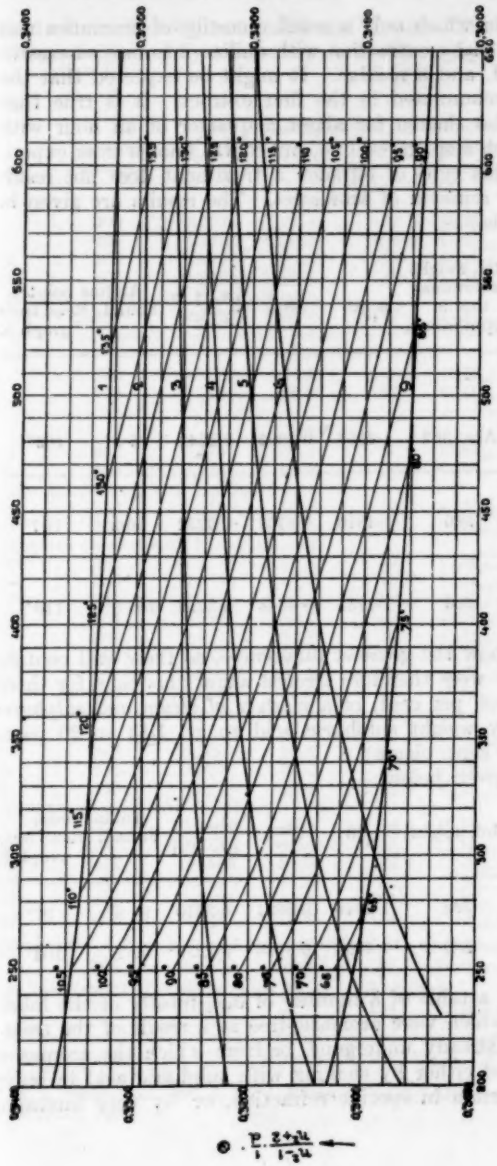


GRAPH 2.

As graph 3 is only applicable to aromatic-free oils, the presence of aromatics will disturb the connection indicated. From the following it is found that a small content of aromatics causes a considerable difference between the aniline point determined and that read. If an oil has been shaken with sulphuric acid and is not yet entirely free from aromatics after the treatment, the specific refraction is then found to be too high (both aromatics and paraffins have a high specific refraction).

The consequence is that an apparently high content of paraffins is calculated, corresponding again to an apparently high aniline point. Actually, however, the aniline point is lowered by the content of aromatics, so that in these cases the difference between the aniline point determined and that deduced is made more pronounced.

[10] It will not be desired either to use graph 2 for deducing the aniline points of pure naphthenes.


MOLECULAR WEIGHT.
1 = Specific refraction of the paraffins (C_nH_{2n+2}).
2 = " " monocycle naphthenes (C_nH_{2n}).
3 = " " dicycle naphthenes (C_nH_{2n-2}).
4 = " " tricycle naphthenes (C_nH_{2n-4}).
5 = " " tetracycle naphthenes (C_nH_{2n-6}).
6 = " " pentacycle naphthenes (C_nH_{2n-8}).
9 = " " polycycle 6-ring naphthenes.

GRAPH 3.

A vaseline oil in which only a small quantity of aromatics was present was divided by extraction with aniline into two successive extracts I. and II. and a residue. It might be expected that the aromatics had accumulated in the first extract. It is true that extract I. was also shaken for about a quarter of an hour with sulphuric acid with a sp. gr. of 1·84, but it was known from experience that with this type of oil such a treatment does not result in a considerable removal of aromatics. The results are given in the following table :—

	Mol. weight determination in naphthaline.	$n_D 20$	$d^{20}/4$	$\frac{n^2-1}{n^2+2}\frac{1}{d}$	Aniline point Found.	Aniline point Read from graph 3.
Extract I. of vaseline oil shaken 15 min. with sulphuric acid .	Abt. 362	1·4892	0·8905	0·3242	87·5°	103°
Extract II. of vaseline oil	380	1·4810	0·8751	0·3252	96·3°	107°
Extract residue of vaseline oil ..	400	1·4755	0·8646	0·3259	103·8°	110°

The extracts show the greatest differences, as these still contain aromatics. They were therefore treated anew, this time for three hours with 300 vol. per cent. of a *mixture of oleum and sulphuric acid* (80 parts by weight sulphuric acid sp. gr. 1·84 to 20 parts by weight 30 per cent. oleum).

The result is given below :—

	Mol. weight.	$n_D 20$	$d^{20}/4$	$\frac{n^2-1}{n^2+2}\frac{1}{d}$	Aniline point Found.	Aniline point Read from graph 3.
Extract I. ..	362	1·4846	0·8921	0·3210	94·8°	97°
Extract II...	380	1·4796	0·8766	0·3239	99·1°	104°

Below is given a table of a number of oils, mostly of the lubricating oil type, which were aromatic-free as a result of the treatments they had already undergone, or from which the aromatics had been removed either by shaking with sulphuric acid in order to attain a minimum in specific refraction, or by very intensive

treatment with sulphuric acid and oleum. The various types of oils are indicated by the letters A, B, C, etc. :—

	Molecular weight.	$\frac{n^2-1}{n^2+2}\frac{1}{d}$	Aniline point (°C) found.	Read from graph 3.	Composition read from graph 3.	Composition calculated from elementary analysis and molecular weight found.
			Group A.			
1 ..	400	0.3221	105.8	103	$C_nH_{2n-3\cdot7}$	—
2 ..	400	0.3218	104.6	103	$C_nH_{2n-3\cdot6}$	—
3a ..	405	0.3232	104.8	106	$C_nH_{2n-3\cdot3}$	—
3b ..	405	0.3232	105.4	106	$C_nH_{2n-3\cdot3}$	—
(3a extra treated with H_2SO_4 oleum).						
4 ..	400	0.3219	106.6	103	$C_nH_{2n-3\cdot6}$	—
			Group B.			
1 ..	530	0.3266	121.8	125	$C_nH_{2n-3\cdot6}$	—
2 ..	513	0.3255	122.0	121	$C_nH_{2n-4\cdot5}$	$C_nH_{2n-3\cdot1}$
			Group C.			
1a ..	350	0.3181	91.2	90	$C_nH_{2n-5\cdot1}$	$C_nH_{2n-5\cdot1}$
1b ..	350	0.3181	91.6	90	$C_nH_{2n-5\cdot1}$	—
(1a extra treated with H_2SO_4 oleum).						
2a ..	352	0.3183	89.6	91	$C_nH_{2n-5\cdot1}$	$C_nH_{2n-4\cdot2}$
2b ..	352	0.3179	90.4	90	$C_nH_{2n-5\cdot3}$	—
(2b extra treated with H_2SO_4 oleum).						
3a* ..	282	0.3170	77.8	78	$C_nH_{2n-4\cdot5}$	—
3b* ..	305	0.3168	82.8	82.5	$C_nH_{2n-5\cdot0}$	—
3c* ..	334	0.3170	86.4	86.5	$C_nH_{2n-5\cdot3}$	—
3d* ..	354	0.3175	88.2	89	$C_nH_{2n-5\cdot5}$	—
3e* ..	380	0.3177	91.9	93	$C_nH_{2n-5\cdot7}$	
3f* ..	410	0.3179	96.0	96.5	$C_nH_{2n-6\cdot0}$	—
3g* ..	451	0.3201	105.3	105	$C_nH_{2n-5\cdot4}$	—
4 ..	362	0.3188	93.6	93	$C_nH_{2n-5\cdot0}$	—
			Group D.			
1 ..	355	0.3202	96.5	94	$C_nH_{2n-4\cdot2}$	$C_nH_{2n-4\cdot0}$
2a ..	350	0.3198	96.6	93.5	$C_nH_{2n-4\cdot3}$	—
2b ..	350	0.3198	96.4	93.5	$C_nH_{2n-4\cdot3}$	—
(2a extra treated with H_2SO_4).						
3 ..	360	0.3194	96.4	93.5	$C_nH_{2n-4\cdot0}$	—
4a* ..	291	0.3180	82.4	82	$C_nH_{2n-4\cdot3}$	—
4b* ..	322	0.3185	87.6	86.5	$C_nH_{2n-4\cdot5}$	—
4c* ..	363	0.3196	94.8	94.5	$C_nH_{2n-4\cdot7}$	—
4d* ..	409	0.3205	101.2	101.5	$C_nH_{2n-4\cdot7}$	—
4e* ..	492	0.3227	113.2	114	$C_nH_{2n-4\cdot2}$	—
Vaseline Oil Aniline Extract I (treated with H_2SO_4 and oleum).						
	362	0.3210	94.8	97	$C_nH_{2n-4\cdot0}$	—
Aniline Extract II (treated with H_2SO_4 and oleum).						
	380	0.3239	99.1	104	$C_nH_{2n-2\cdot7}$	—

* Fractions obtained by cathode light vacuum distillation according to the improved method of H. I. Waterman and E. B. Elsbach, "Chemisch Weekblad" 1929, **26**, 468.

H. I. Waterman and J. N. J. Perquin, Technical Analyses, 4th Edition, Dordrecht, 1931.

The elementary composition determined and that deduced agree very well. *It will be simpler to deduce the elementary composition from n_d density and molecular weight than to make an elementary analysis.* In order to deduce the series formula from this analysis it is necessary, however, to know the molecular weight.

With the aid of the above-described method the work of other investigations can be criticised. For instance, in an article by S. Kyropoulos, "Physikalische Eigenschaften und Konstitution der Mineralschmieröle"[11] (physical properties and constitution of mineral lubricating oils), in which valvoline oil is examined as an example of a paraffinous oil, it is found that this oil is to be classified as a mixture of iso-paraffin, which is deduced from the absolute values of n_d and density in connection with the molecular weight. From the data regarding the specific refraction it can be shown at once that Kyropoulos' conclusions in regard to the chemical nature of lubricating oils and certain hydrocarbons must certainly be incorrect.

The following are a few examples :—

	Mol. weight.	n_d^{20}	$d^{20}/4$	$\frac{n^2-1}{n^2+2}\frac{1}{d}$	Specific refraction of the corresponding paraffin.	Described by Kyropoulos as being :
Valvoline oil H. ..	603	1·4884	0·8818	0·3268	0·3319	isoparaffin.
The too low specific refraction indicates the presence of naphthenes.						
Valvoline oil PH.G.VI.397		1·4815	0·8857	0·3216	0·3332	isoparaffin.
The low specific refraction indicates the presence of a large quantity of naphthenes.						
$C_{14}H_{32}(C_nH_{2n})$ ..	224	1·4510	0·8254	0·3262	0·3361	isoparaffin.
Naphthenes must be present in this oil.						
$C_{19}H_{36}(C_nH_{2n-2})$ ..	264	1·4614	0·8771	0·3131	0·3351	isoparaffin.
Presumably naphthenes are mainly present.						
$C_{13}H_{26}(C_nH_{2n})$ ..	182	1·4745	0·8134	0·3458	0·3379	naphthene.

(It is impossible that many naphthenes are present in this oil, the specific refraction being much too high. Presumably it is a mixture of aromatics and (iso)paraffins.) Kyropoulos certainly makes use of the molecular refraction for checking his observations, but the graph used by him is on much too small a scale, so that the conclusions must be misleading. This is also pointed out by W. Bielenberg.[12] On the other hand, however, the results of other researchers' work tallies exactly or almost so with the conclusion arrived at from our own observations. In this connection we may refer to M. Bestushew.[13]

[11] *Z. Phys. Chem.*, 1929, **144**, 22–48.
[12] *Z. Phys. Chem.*, 1930, **149**, 42.
[13] *Erdöl und Teer (Chem. Techn.)*, 1931, **7**, 159.

	$d^{15°}$	n_D	$\frac{n^2-1}{n^2+2}\frac{1}{d}$	Engler viscosity at 50° C.	Number of C atoms calculated from elementary analysis.	Molecular weight determined.	Series determined from elementary analysis.	Series read from diagram of specific refraction and molecular weight (graph 3).	Aniline point determined experimentally.	Aniline point read from graph 3. from $\frac{n^2-1}{n^2+2}\frac{1}{d}$ and molecular weight.	Aniline point read from graph 3. from* elementary composition and molecular weight.
					Naphthenes from Grosny Crude Oil.						
Fraction I	0·826	1·4527 (24°)	0·3295	1·27	18·7	262	C_nH_{2n}	C_nH_{2n}	93·6	97	97
,, II	0·839	1·4592 (22°)	0·3279	1·44	20·9	292	C_nH_{2n-6}	C_nH_{2n-6}	97·4	99	99
,, III	0·862	1·4710 (20°)	0·3256	2·32	26	363	C_nH_{2n-14}	C_nH_{2n-14}	104·8	106	106
,, IV	0·874	1·4751 (22°)	0·3240	4·23	28·1	392	C_nH_{2n-16}	C_nH_{2n-14}	108·4	106	107
					Naphthenes from Dossor Oils.						
Fraction I	0·867	1·4768 (15°)	0·3256	1·8	22·9	319	C_nH_{2n-12}	C_nH_{2n-12}	96·4	100	98
,, II	0·877	1·4813 (15°)	0·3247	4·9	33·4	469	C_nH_{2n-8}	C_nH_{2n-8}	113·4	115	118
					Naphthenes from Balachany Crude Oil.						
Fraction I	0·851	1·4675 (19°)	0·3274	1·38	17·5	244	C_nH_{2n-6}	C_nH_{2n-6}	87·9	89	87
,, II	0·889	1·4824 (20°)	0·3222	4·0	24·1	336	C_nH_{2n-14}	C_nH_{2n-14}	100·2	96	97·5
,, III	0·897	1·4888 (21°)	0·3232	8·1	26·5	368	C_nH_{2n-18}	CnH_{2n-8}	105·8	102	101
,, IV	0·899	1·4890 (21°)	0·3225	10·1	28·8	400	C_nH_{2n-8}	CnH_{2n-16}	110·2	104	103
					Naphthenes from Maikop Crude Oil.						
Fraction I	0·841	1·4624 (15°)	0·3271	1·39	20	278	C_nH_{2n-6}	CnH_{2n-6}	92·8	95·5	88
,, II	0·872	1·4736 (20°)	0·3234	3·32	27·3	379	C_nH_{2n-14}	C_nH_{2n-14}	—	103	103
,, III	0·889	1·4802 (17°)	0·3202	5·83	31·4	437	C_nH_{2n-16}	C_nH_{2n-16}	113·0	104	108
					Naphthenes from Kalushsky Crude Oil.						
Fraction I	0·864	1·4683 (19°)	0·3230	1·31	17·5	244	C_nH_{2n-6}	CnH_{2n-8}	81	82	83·5
,, II	0·866	1·4696 (19°)	0·3230	1·51	19·9	277	C_nH_{2n-12}	C_nH_{2n-12}	88·1	88	88
,, III	0·882	1·4783 (18°)	0·3219	2·64	24·6	341	C_nH_{2n-12}	C_nH_{2n-12}	97·6	96·5	97
,, IV	0·899	1·4831 (18°)	0·3185	4·95	28·1	390	C_nH_{2n-6}	C_nH_{2n-16}	102·6	96	101·5
,, V	0·908	1·4868 (18°)	0·3174	7·63	29·8	413	C_nH_{2n-16}	C_nH_{2n-16}	105	96	102·5
					Naphthenes from Surachany Oils.						
Fraction I	0·840	1·4603 (23°)	0·3284	1·41	19·4	270	C_nH_{2n-6}	C_nH_{2n-6}	93·8	97	86

* Series determined from elementary analysis (column 8).

In order to ascertain the structure of lubricating oil naphthenes and aromatics he treats fractions from various Russian oils with concentrated sulphuric acid (98–100 per cent.). If necessary free paraffins are first removed with butanone or with a mixture of ether and alcohol. Bestushew determined the specific gravity, the index of refraction, the viscosity, the aniline point, the molecular weight and the elementary analysis of the original fractions and of the naphthenes from those fractions. From the last two constants the series formula can be calculated.

From his data for n and d we calculated the specific refraction (after having converted this, where necessary, at the same temperature). With the aid of this specific refraction and the molecular weight, the elementary composition and the aniline point can be read from graph 3, whilst the aniline point is also deduced from the elementary composition found by Bestushew (see table).

The conformity between the aniline point determined experimentally and that deduced from the specific refraction is, in general, very good, although there are some deviations. In the case of fraction I. from Maikop crude oil and fraction I. from Surachany oil the elementary analysis is probably incorrect. Not only is the aniline point deduced from the formula stated much too low (see last column), but when the fractions in question are compared with fraction II. from Grosny oil, with which the constants all closely agree, there is found to be a deviation in the elementary composition.

In the case of fractions IV. and V. from Kalushky crude oil an error in the specific refraction (thus in n_d or density) is more likely, as aniline points deduced therefrom show deviations.

These observations will also be extended in the near future to other constants.

Finally we wish to express our thanks to the Management of the Bataafsche Petroleum Maatschappij for their kind permission to publish this article.

The Knock Rating of Naphthene and Aromatic Hydrocarbons.*

By F. H. Garner, Ph.D., M.Sc., F.I.C. (Member) and E. B. Evans, M.Sc., A.I.C. (Assoc. Member).

Summary.

The knock rating determinations at 212° F. and 300° F. jacket temperature are given on eight hydrocarbons of the cyclohexane series and six hydrocarbons of the cyclopentane series, together with a summary of seven aromatic hydrocarbons investigated in the present work and nine aromatic hydrocarbons previously investigated.

1. In the cyclohexane and cyclopentane series, the octane number decreases as the number of carbon atoms in the molecule is increased.

2. In the aromatic hydrocarbon series the octane number increases until the member of the series containing 9 carbon atoms is reached, and in general the octane number of aromatic hydrocarbons is less affected by substitution in so far as knockrating is concerned than other series of hydrocarbons.

3. Lovell, Campbell and Boyd's rule that the more centralised the molecule the higher the octane number holds in the case of the cyclopentane, cyclohexane and aromatic hydrocarbons investigated in the present paper.

4. The octane number at 300° F. shows lower figures than at 212° F. with the lower members of the series, but in the higher members of the series the octane number is greater at 300° F. than at 212° F.

5. It is shown that in so far as the increase in octane number is concerned when lead is added to the members of the various hydrocarbon series that the increasing order of susceptibility is: aromatics, cyclohexanes, cyclopentanes and most responsive of all, α-olefines.

In the development of methods for the determination of the knock rating of gasolines during the last fourteen or fifteen years, considerable attention has been devoted to the relative knock rating of the individual hydrocarbons and hydrocarbon series present in gasoline. In a recent paper[1] a brief historical summary has been given of the work on this subject previously recorded, and it may be noted that hitherto but little information has been available concerning the knock ratings of the naphthene hydrocarbons, and has indeed been confined to the first three members of the cyclohexane series. The present paper gives the results of the examination of eight cyclohexane hydrocarbons and six cyclopentane hydrocarbons. The knock ratings have been determined at two temperatures, namely 212° F. and 300° F., as octane numbers of 20 per cent. volume solutions of the hydrocarbon in a standard

* Paper received July 1, 1932.

fuel. The S.30 engine was used, and is particularly suitable for the purpose as only a relatively small amount of fuel is required for a determination.

In addition to the octane numbers at two jacket temperatures, the susceptibility to lead tetraethyl of the 20 per cent. solution was also determined at 212° F., and in a few instances at 300° F.

Knock rating determinations were also made on a number of aromatic hydrocarbons which had not hitherto been investigated, and a summary is given of previous knock rating determinations of aromatic hydrocarbons on the Delco engine. The present paper, therefore, deals essentially with the knock ratings of the cyclic hydrocarbons present in gasoline, and shows the susceptibility of these hydrocarbons to variation in jacket temperature, and to lead tetraethyl.

Aromatic Hydrocarbons in Petroleum.

The presence of aromatic hydrocarbons in petroleum was first shown by de la Rue and Müller in an examination of Burmese petroleum described in the Proceedings of the Royal Society in 1856.[2] Several tons of "Rangoon Tar" were steam distilled, a further separation effected by repeated fractional distillation, and the aromatic hydrocarbons converted into nitro-compounds by means of a mixture of sulphuric and nitric acids. These authors showed the presence of benzene, toluene, xylene and cumene in Burmese naphtha. Within ten years of the publication of this work, the presence of aromatic hydrocarbons was shown in Galician crude by Pebal,[3] in Pennsylvanian crude by Schorlemmer,[4] and in Hanoverian crude by Bussenius and Eisenstock.[5] Later, Markownikoff, Mabery and other workers showed that aromatic hydrocarbons were normal constituents of petroleum, and at a much later date, in 1907, H. O. Jones and Wootton[6] drew attention to Borneo petroleum, which contains an exceptionally large proportion of aromatic hydrocarbons.

Although the presence of aromatic hydrocarbons in petroleum has thus been known for seventy-five years, comparatively little data has been published on the relative proportions of aromatic hydrocarbons present. It is, however, known that these may vary from 2 per cent. in natural gasoline, up to 40 per cent. in the gasoline fractions of some Far Eastern crudes.

We give in the table below, figures showing the percentage of aromatic hydrocarbons present in a large number of gasolines, together with the percentage of gasoline obtained from the crude petroleum, where the latter figure was available. In most cases, about 30 per cent. of the gasoline distilled over at 100° C. The percentages of benzene, toluene and xylenes present in these

gasolines are given, and it will be noted that in nearly every case, the percentage of benzene is the lowest, of toluene intermediate, and of xylenes the highest. It is interesting to note that in the work of Bussenius and Eisenstock[5] (1860) a greater proportion of xylenes than toluene was evidently present in Hanoverian crude.

The estimation of the aromatic hydrocarbons were carried out on carefully fractionated samples of the gasoline, the cutting points being 60° C.–90° C. for benzene, 90–122° C. for toluene and 122–150° C. for xylenes. It will be appreciated that with a gasoline showing as much as 30 per cent. over at 100° C. the fraction 122–150° C. does not always represent the total proportion present in the crude petroleum, and therefore, that the percentage of xylenes given is, in some instances, relatively low in comparison with the percentages of the two lower aromatic hydrocarbons.

In every case but one, the concentration of the aromatic hydrocarbons in the *individual* fractions increases with increase in boiling point of the fraction. There is, however, one point of special interest in the Table I., namely, the Mexia crude petroleum, which shows a high percentage of benzene compared with that of toluene and in which the concentration in the individual fractions was found to be :

Benzene	27%
Toluene	22%
Xylene	19%

In order to obtain the percentage of benzene in the *gasoline* the figure of 27 per cent. given here must naturally be multiplied by the percentage of gasoline distilling between 60–90° C. in the fractional distillation. With all other crude petroleums examined, the concentration of aromatic hydrocarbons in the individual fractions, increases with increasing boiling-point. If reference is made to the Report of Investigation No. 2203 (1921), published by the U.S. Bureau of Mines, it will be seen that the lower fractions of Mexia crude (Sample No. 795), have relatively high specific gravities, although the kerosine and lubricating oil fractions are typical of the Midcontinent Field crude petroleums.

The general conclusion which can be drawn from the Table I. is that in gasolines from paraffin and naphthene base petroleums, the percentage of aromatic hydrocarbons is low (e.g., Pennsylvanian gasoline contains only about 3 per cent. total aromatics, and Baku about 1.5 per cent.). Higher percentages are generally present in mixed base crude petroleums and petroleums of high asphalt content. The Borneo crude must be considered as being in a separate category as nearly 40 per cent. of aromatic hydrocarbons is present in the gasoline fraction.

The figures given below are quoted according to the field of origin, but it will be appreciated that in some cases they apply to only one particular area of the field. The last four figures in the Table are quoted from the literature.

TABLE I.

Aromatic Hydrocarbon Content of Petrols by Weight.

	Hardstoft (English).	Powell.	Reagan.	Seminole.	Grosny.	Peruvian.
Yield of Gasoline	4%	16%	35%	36%	13%	20%
Benzene ..	0·15	0·4	0·1	0·1	0·4	0·3
Toluene ..	0·5	1·2	0·2	0·6	1·4	1·6
Xylenes ..	1·3	2·9	1·5	1·5	2·0	2·5
Total Aromatic hydrocarbons up to 150° C.	1·95	4·5	1·8	2·2	3·8	4·4

	Mexican.	Panuco.	Venezuelan.	Colombian.	Californian.	Persian.
Yield of Gasoline	10%	3%	7%	20%	20%	30%
Benzene ..	0·5	0·7	0·9	0·2	0·6	1·5
Toluene ..	1·5	1·9	1·5	0·8	2·4	4·5
Xylenes ..	3·0	4·0	3·7	1·3	3·7	5·1
Total Aromatic hydrocarbons up to 150° C.	5·0	6·6	6·1	2·3	6·7	11·1

	Heavy. Smackover.	Mexia.	Roumanian.	Baku.	Borneo.[7]	Miri.[7]	Burmah.[8]	Badarpur.[8]
Benzene ..	0·15	5·0	1·8	0·04	7·0	0·4	2·9	1·0
Toluene ..	0·4	8·0	3·6	0·8	14·0	1·9	6·0	1·6
Xylenes ..	1·5	4·5	4·2	0·6	15·0	1·5	6·8	2·9
Total Aromatic hydrocarbons up to 150° C.	2·05	17·5	9·6	1·44	36·0	3·8	15·7	5·5

The Borneo gasoline contained only about 20 per cent. and the Miri only 7 per cent., distilling over at 100° C.

No estimate is given of the percentage of higher aromatic hydrocarbons distilling over 150° C. present in these gasolines, but in those instances in which we have data the concentration in the fraction is higher than that of the xylenes.

A very large number of individual aromatic hydrocarbons have been shown to be present in petroleum, and amongst those present in gasoline fractions are benzene and toluene, o-, m-, and p-xylenes, pseudocumene, p-cymene, diethylbenzene, two tetramethylbenzenes and isoamylbenzene.

Naphthene Hydrocarbons in Petroleums.

There occur in all known petroleums the cyclic saturated hydrocarbons to which Markownikoff and Oglobin[9] applied the name "naphthenes." These hydrocarbons are chiefly the alkyl derivatives of cyclopentane and cyclohexane and represent a considerable proportion of the light fractions of petroleum.[10]

A great deal of confusion existed at first as regards the constitution of even the simpler naphthenes in petroleum. It was thought (cf. Beilstein and Kurbatow[11]) that these compounds were all derivatives of cyclohexane. Kishner,[12] however, showed that the so-called "hexahydrobenzene," separated from petroleum and prepared by reduction of benzene with hydriodic acid (Wreden[13]), was really methyl cyclopentane. Shortly afterwards, Markownikoff[14] isolated cyclohexane from Baku petroleum and showed its identity with the synthetic product made by Baeyer[15] from succinyl-succinic acid. It was then realised that at least two ring systems (penta- and hexa-) occur in petroleum.

Naphthenes containing rings of four, five, six, seven, eight and nine carbon atoms have been stated at various times to have been identified in petroleum. Thus, cycloheptane was considered to occur in Caucasian naphtha by Markownikoff. The same author also thought cyclobutane occurred in the pentane fraction of Russian petroleum, but on very slender evidence. A dimethyl cyclobutane has also been reported to occur in Californian oil (Brooks[16] states that Midgley has isolated this compound).

Zelinsky[17] has also shown that various hydrocarbons, termed "heptanaphthenes" and "octanaphthenes" by Markownikoff on purely analytical data, are in reality alkylated penta- or hexamethylenes; *e.g.*, Markownikoff's "octanaphthene" b. pt. 119° C. is 1-3 dimethyl cyclohexane.

Petroleum, formed under conditions involving long heating under pressure, would naturally be expected to contain compounds containing the most stable types of ring structure. According to the strain theory of Baeyer, the most stable of the unsubstituted polymethylenes is cyclopentane, with cyclohexane not quite so stable, and cyclobutane and cycloheptane in a state of considerable strain. The stability of the hydrocarbon depends not only on the number of carbon atoms in the ring, but also on the nature and position of the substituent radicles. Thorpe[18] and his co-workers have shown that the presence of substituents of large atomic volume affects the ease of formation and stability of rings. A gem-dimethyl group, for instance, increases the stability of cyclopropane and cyclobutane rings, but would be expected to decrease the stability of a cycloheptane ring, as in this case the substituent would tend to force the angle of the valencies back from 128°34′ to

the natural angle of 109°28′; in the case of cyclobutane the group would help to maintain the angle of 90° assumed by reason of ring-formation. It would thus be anticipated that substituted cyclobutanes are of more probable occurrence in petroleum than cycloheptane derivates. The majority of the compounds present, however, are likely to be of the less-strained five or six ring types. In view of the special attention now being given to experimental work on the stability of various types of hydrocarbons under varying conditions of pressure and temperature, valuable information will be available as regards the types of hydrocarbons which would be expected to be present in petroleum, not only as regards naphthenes, but also concerning the branched and normal paraffin hydrocarbons.

A considerable number of naphthene hydrocarbons have been isolated by various workers from the light fractions of petroleum. Prominent among these workers are Markownikoff, Zelinsky, Young and Fortey, and Mabery. Some of the simpler hydrocarbons of the cyclohexane and cyclopentane series, such as the methyl- dimethyl- and ethyl- derivatives have been proved to be present in petroleum, and definite indications of the presence of other hydrocarbons of these series have been obtained. The evidence in support of the presence of naphthene hydrocarbons other than those of the cyclohexane and cyclopentane series is, however, very slender.

An important investigation on the occurrence of hydrocarbons in petroleum is that which is now being made by Washburn, Bruun, Hicks-Bruun, Schicktanz and others.[19] These authors have undertaken a systematic separation of the compounds in a crude petroleum from the South Ponca field of Oklahoma, and have isolated hydrocarbons in a state of purity, at the same time determining the percentage of the individual hydrocarbons present. The results so far published are summarised in Table II.

TABLE II.

Hydrocarbon.	Percentage Present based on Crude.	Percentage of Spirit Fraction. Assuming 25% yield.	Assuming 40% yield.
n-Hexane	0·33	1·3	0·8
2-Methylpentane	0·09	0·4	0·2
3-Methylpentane	0·18	0·7	0·5
2-3-Dimethylbutane ..	0·04	0·15	0·1
n-Heptane	0·9	3·6	2·25
n-Octane	1·0	4·0	2·5
n-Nonane	1·0	4·0	2·5
n-Decane	0·6	2·4	1·5
Benzene	0·08	0·3	0·2
Toluene	0·33	1·3	0·8
Methylcyclopentane ..	0·2	0·8	0·5
Cyclohexane	0·33	1·3	0·8
Methylcyclohexane ..	0·3	1·2	0·75
Per cent. so far accounted for	5·38	21·45	13·4

Considerable progress has thus been made towards the elucidation of the composition of the gasoline fraction of this Mid-Continent crude petroleum, and it will be seen that noteworthy proportions of aromatic and of both cyclopentane and cyclohexane hydrocarbons are present.

Considerable light has been thrown on the proportions in which cyclopentane and cyclohexane hydrocarbons occur in petroleum by a long series of investigations by Zelinsky and his co-workers, dating back some twenty years. Zelinsky has shown that by two or three passages of petroleum vapour over platinum black or platinised charcoal, the hexahydrobenzene derivatives can be completely dehydrogenated and removed by sulphonation of the aromatics thus formed. It should be noted that only those six-membered ring compounds which can be regarded as hexahydro-aromatics can be dehydrogenated by this method.[20] Thus 1-1, dimethyl-cyclohexane could not be dehydrogenated. The cyclo-pentane nucleus is stable to this dehydrogenation process and consequently the naphthenes left after removal of the hexahydro-aromatics must be mainly cyclopentane derivatives. In this way[21] the 102-104° C. fraction of Baku benzine was shown to consist chiefly of methyl cyclohexane (about 50 per cent.) and ethyl cyclopentane. Similarly[22] the 170-200° C. fraction contains about 30 per cent. of hexahydroaromatics, the remainder being chiefly cyclopentane derivatives.

The composition of Ural and Surachany benzines is described in a paper by Zelinsky and Juriev[23], both being shown to contain hexahydroaromatics. The so-called "octanaphthene" (b. pt., 120° C.) and "nonanaphthene" (b. pt., 137° C.) from Caucasian petroleum, are probably cyclopentane derivatives.[24]

Manning and Shepherd[25] have applied the dehydrogenation method of Zelinsky to the determination of cyclohexane derivatives in spirits from the carbonisation of coal.

The importance of cyclopentane derivatives in petroleum is further shown by the work of Zelinsky and Chuksanov[26], who prepared a series of cyclopentane hydrocarbons from naphthenic acids from Baku petroleum and showed that only small proportions of cyclohexane derivatives were present in these naphthenic acids. Von Braun and his collaborators[27] have confirmed this conclusion and have definitely shown that naphthenic acids are mainly carboxylic acids of cyclopentane hydrocarbons. Petrov and Ivanov[28] consider that these acids are formed in part by the oxidation of naphthenes and polynaphthenes in air, and the constitution of these acids thus serves as an indication of the types of hydrocarbons probably present in crude petroleums.

The foregoing remarks indicate clearly that the naphthenic hydrocarbons are important constitutents of petroleum spirits, and further that these consist essentially of derivatives of cyclopentane and cyclohexane, the occurrence of other ring systems not having definitely been proved. The information available concerning percentages of these two series present is very meagre, but does indicate that the cyclopentane series is of equal importance with the cyclohexane series.

Previous Work on the Knock Rating of Cyclic Hydrocarbons.

Ricardo determined the highest useful compression ratio of benzene, toluene and xylene on the E.35 variable compression engine in work carried out from 1919–23[29] and published in the Empire Motor Fuels Committee Report. His results indicated that toluene was better than benzene, but that xylene was slightly worse than toluene. The xylene which he employed, however, contained only 91 per cent. aromatics. Midgley and Boyd[30] made a comparison of the same hydrocarbons in kerosine, and concluded that the order of increasing anti-knock value was benzene toluene and xylene. Ricardo (*loc. cit.*) also investigated three derivatives of cyclo-hexane, namely, cyclohexane, methyl-cyclohexane and a mixture of dimethyl-cyclohexanes, but the purity of these hydrocarbons was very low and in the case of the dimethyl-cyclohexane only 60 per cent. of naphthenes were present. The figures which he obtained are given in Table III. below :—

Table III.

Hydrocarbon.	Variable Compression Engine. H.U.C.R.	Variable Compression Engine. Toluene Value.	Supercharged Engine. Toluene Value.
Benzene	6·9*	(67)	(66)
Toluene	>7·0	100	100
Xylene	>7·0	(85)	(83)
Cyclohexane	5·9*	35	38
Methylcyclohexane ..	5·8	31·5	·28
Hexahydroxylenes ..	4·9	1·5	2·5
Heptane	3·75	—37·0	—

* Denotes pre-ignition.

( ) Denotes extrapolated values from blends of the hydrocarbon with an aromatic-free gasoline of which the H.U.C.R. was 4.85 and the toluene value 0.

Howes and Nash[31] have published the results of a series of knock rating determinations made on a solution of 20 per cent. of various aromatic hydrocarbons in a standard gasoline. These results were determined on a Delco engine and as they were carried out under similar operating conditions and in the same laboratory as the determinations given in this paper, the complete results are quoted in the discussion later.

Egloff and Morrell[32] deduced from Ricardo's results that the relative effectiveness of aromatics, naphthenes and unsaturated hydrocarbons in suppressing tendency to knock is in the ratio 20 : 5 : 4.

Stevens and Marley[33] using toluene, methylcyclohexane and hexylene as typical hydrocarbons, and the Delco engine fitted with bouncing-pin, obtained a ratio of 2 : 1 : 1. The comment is made that in using this ratio to evaluate petroleum spirits, no account is taken of the possible presence of cyclopentane derivatives. The fifteen aromatics and fourteen naphthenes tabulated later in the present paper, show that the ratio of the average blending octane numbers at 212° F. (114 and 59) is close to the ratio 2 : 1.

Callender, King and Sims[34] state that additions of 5 per cent. by volume of hydrocarbons to a fuel of H.U.C.R. of 4·9 produced the following increase of H.U.C.R. :—

Benzene	1·0%
Toluene	2·0%
o-xylene	0·6%
Pseudo-cumene	−0·4%

The decrease of H.U.C.R. for pseudo-cumene is surprising, as all the aromatics reported in the present paper have very high octane numbers.

Another scale has been employed for expressing results on cyclohexane and on benzene by Birch and Stansfield.[35] A 20 per cent. by weight solution of cyclohexane in a certain reference fuel is stated to be equivalent to a blend of 39 per cent. of n-heptane and 61 per cent. of benzene (both by volume), while 20 per cent. weight of benzene in the same fuel was equivalent to a 38·8–61·2 per cent. volume blend of heptane-benzene. The effects of benzene and cyclohexane are roughly equal on a weight basis : 20 per cent. by weight corresponds to about 19·0 per cent. by volume for cyclohexane and 17·1 per cent. for benzene, and thus benzene is slightly more effective than an equal volume of cyclohexane. These authors also state that the increasing order of anti-knock value of the aromatics is benzene, toluene, ethylbenzene and propylbenzene, but xylene is said to be inferior to ethylbenzene. No experimental figures are given for the higher aromatic hydrocarbons.

Recently, Lovell, Campbell and Boyd[36] stated that benzene has a value, on their aniline equivalent scale, of +10, heptane being −14 and iso-octane +16 on the same scale.

Since the completion of this paper, some work has recently been published by Schmidt and others,[37] giving the results of knock-rating measurements on pure hydrocarbons in 30 per cent. volume solution in a Grosny benzine of H.U.C.R. 4·84. A variable compression engine was used and the results are, unfortunately,

expressed in terms of the H.U.C.R. of the mixture instead of octane number; those of interest, so far as the present paper is concerned, are given below :—

Hydrocarbon.	H.U.C.R.
Benzene	5·33
Toluene	5·56
Xylene	5·77
Ethylbenzene	5·42
Cyclohexane	4·96
Methylcyclohexane	5·18
Hexahydroxylene	5·33
Ethylcyclohexane	5·05

It will be seen that in the case of the aromatics, toluene is apparently better than either benzene or ethylbenzene, xylene being better than toluene. A similar order is observed in the cyclohexane series, the methyl derivative being better than either cyclohexane or ethylcyclohexane, and hexahydroxylene being best of all. No differences could be detected due to position isomerism in the xylenes or dimethyl cyclohexanes. As will be seen later, we find that cyclohexane has the highest anti-knock value of this series which is contrary to the results obtained by Schmidt, who finds that methyl cyclohexane is better than either cyclohexane or ethyl cyclohexane. It will also be noted that in the aromatic series the relative order of the hydrocarbons tested by Schmidt is different from that obtained by Birch and Stansfield (*loc. cit.*); our own determinations for these hydrocarbons agree with those of the latter investigators.

Apart, then, from these more or less isolated results on different scales and under different conditions of measurement, the experiments recorded here represent the first published attempt to present a systematic study of the detonation values of the cyclic hydrocarbons.

The Preparation of Hydrocarbons used in this Investigation.

One of the principal difficulties associated with the determination of the knock ratings of pure hydrocarbons, arises from the quantity of material required for the measurements. Even with a test-engine of low volumetric capacity such as the S.30 engine, the quantity of fuel needed for three or four measurements is generally more than 500 ml. Working with 20 per cent. by volume solutions of the hydrocarbon in a reference fuel, more than 100 ml. of each hydrocarbon are required, assuming that the engine tests are made under ideal conditions.

Most of the hydrocarbons used in this work were synthesised, using the methods described briefly below, but a few were purchased and further purified before use.

Cyclopentane hydrocarbons.—For the preparation of cyclopentane adipic acid was used as the starting material. This was distilled with baryta to give cyclopentanone,[38] the latter being reduced by sodium in moist ether to give cyclopentanol. Dehydration of the alcohol with zinc chloride gave cyclopentane, which hydrogenated readily in glacial acetic acid solution in the presence of platinum black[39] yielding cyclopentane. The methyl-, ethyl-, n-propyl- and n-butyl- cyclopentanes were obtained as described by Chavanne and Becker.[40] Cyclopentanone was treated with the appropriate alkyl magnesium halide and the resulting alcohol dehydrated; p-toluene sulphonic acid was found to be the most satisfactory reagent for this purpose. The alkyl-cyclopentene was carefully fractionated and then hydrogenated, as in the case of cyclopentene itself, to the corresponding cyclopentane; the latter was treated with 99 per cent. sulphuric acid, washed and fractionated. 1-3 dimethyl-cyclopentane was prepared similarly, but using β-methyl adipic acid as a starting material. This was converted into 3-methyl cyclopentanone,[41] and the dimethyl derivative obtained by a similar method to that used for the monomethyl cyclopentene. The yields of the purified cyclopentane hydrocarbons were in general 20–30 per cent. calculated on the weight of cyclopentanone used.

Some divergency exists between the figures given in the literature for the physical constants of the cyclopentane hydrocarbons (cf. Chavanne and Becker[40] and Eisenlohr[43]). The data obtained on our samples are recorded below. They agree in most cases excellently with those given by Chavanne, but differ somewhat from those of Eisenlohr. The figures given in the last line of the tables are aniline points and not critical solution temperatures, and, as might be expected, they are a little lower than Chavanne's data. The aniline points for the cyclopentene hydrocarbons have not previously been recorded. The results of the iodine number determinations are also interesting. Cyclopentene itself shows, using Hanus solution, a value which is almost theoretical. The values for all the other members of the series are in excess of the theoretical, indicating probable oxidation with rupture of the ring.

TABLE IV.

Properties of the Cyclopentane Hydrocarbons.

Hydrocarbon.	Cyclo-pentane.	Methyl cyclo-pentane.	Ethyl cyclo-pentane.	1-3-Dimethyl cyclo-pentane.	n-Propyl cyclo-pentane.	n-Butyl cyclo-pentane.
Boiling Pt. (corrd.) ..	49·4—0·5	71·9	103·0 ± 0·5	90·5	130·6 ± 0·2	157·2
$d\frac{15}{4}$	0·7498	0·7541	0·7736	0·7504	0·7812	0·7886
$d\frac{20}{4}$	0.7457	0.7496	0.7695	0.7463	0.7766	0.7847
$n\frac{20}{D}$	1·4070	1·4099	1·4201	1·4096	1·4269	1·4310
Iodine No.	0·2	0·2	0·3	0	0	1·0
Aniline Point ..	16·8° C.	33·0	36·7	46·4	44·5	48·7

TABLE V.

Properties of the Cyclopentene—1 Hydrocarbons.

Hydrocarbon.	Cyclo-pentene.	Methyl cyclo-pentene	Ethyl cyclo-pentene	n-Propyl cyclo-pentene.	n-Butyl cyclo-pentene.
Boiling Pt. (corrd.) ..	44·5+0·1	75·5+0·1	100·5+0·1	131·7+0·5	157
$d\frac{15}{4}$	—	0·7848	0·8041	0·8065	0·8107
$d\frac{20}{4}$	—	0·7814	0·7993	0·8024	0·8073
$n\frac{20}{D}$	1·4262	1·4317	1·4411	1·4435	1·4475
Iodine No.	377	337–401	321–366	309–334	264–293
.. (Theor.) ..	373	310	264	231	205
Aniline Point ..	Below —10° C.	—7·0 °C.	+1·2°	+14·2°	+25·0°

Cyclohexane hydrocarbons.—Cyclohexane was purchased from Howards & Sons, Ltd., and purified by an exhaustive treatment with 99 per cent. sulphuric acid, followed by fractionation through an efficient column, a final fraction boiling over 0·2° C. being collected. The sample was not quite pure, judged by comparison with the figures recently given by Bruun and Hicks-Bruun.[44] Their results indicate, however, that a sample of freezing point 4·5° C. is of nearly 99·5 per cent. purity. Methylcyclohexane was obtained from the same source and similarly purified, but in this case the boiling range of the material obtained after several fractionations was about 1° C.; the constants are, however, in quite good agreement with those quoted in a paper by Bruun and Hicks-Bruun.[45] Ethyl-, n-propyl and n-butyl-cyclohexanes were obtained by the hydrogenation of the corresponding aromatic derivatives (see below) in glacial acetic acid solution and in the presence of platinum black.[46, 47] The reaction was generally rather slow, but proceeded almost to completion; small amounts of unchanged aromatic compounds were removed by treatment with sulphuric acid and the product carefully fractionated.

The ortho-, meta-, and para-dimethyl cyclohexanes were purchased from Rhône-Poulenc, Paris. These samples are, of course, mixtures of the cis- and trans-isomers, since these compounds exhibit the phenomenon of stereo-isomerism, in common, doubtless, with many other hydrocarbons occurring in petroleum. The properties of the two modifications are, according to Eisenlohr, (*loc. cit.*) quite different—the trans-isomer is stated to boil some two degrees lower than the cis form, and the density of the former is also lower. The products from Rhône-Poulenc had boiling ranges of about 2° C. and correspond fairly closely in this respect with Eisenlohr's values for the cis forms. The densities are, however, higher in every case than those of Eisenlohr's cis form. A further remarkable point is that the meta- and para-compounds (*i.e.*, mixtures of isomers) are almost identical as regards density,

boiling-point, refractive index and aniline-point. They differ, however, in their freezing-points and also in their viscosities. It is not, however, thought that the cis- and trans-isomers are likely to differ appreciably in their detonation behaviour in an engine.

The figures given in the literature for the physical constants of the cyclohexane hydrocarbons are not, in general, in very good agreement, differing in the density for example, by several units in the third decimal place. The products of which the constants are given in the following tables have been prepared from carefully purified aromatic hydrocarbons (in the cases of the ethyl, n-propyl and n-butyl members) and further sulphonated and fractionated after hydrogenation. The figures given for the properties of the ethyl-, n-propyl-, and n-butyl-cyclohexanes are, therefore, considered of definite value as representing the pure hydrocarbons.

Aromatic hydrocarbons.—Benzene and toluene used in this work were A.R. quality materials purchased from the British Drug Houses, Ltd.

Ethylbenzene was obtained from Baird & Tatlock, Ltd. The material, initially of good quality, was carefully re-fractionated, a fraction boiling wholly within 1° C. being finally selected.

n-Propylbenzene was prepared by the method described by Gilman and Meyers.[48] The maximum yield obtained after purification by long refluxing over sodium wire and subsequent fractionation was about 53 per cent. theoretical, the product boiling at 158·6 ±·7° C. Repeated fractionation did not seem to narrow this range appreciably.

The Wurtz reaction was employed in the synthesis of n-butylbenzene. Radziswewski[49] stated that an almost theoretical yield of the desired hydrocarbon was obtained by heating benzyl chloride and propyl bromide, together with sodium, for several hours on the sand-bath. It is highly improbable from the nature of the reaction that this was the case, and actually, as might be expected, our experiments showed that much dibenzyl was formed together with some n-hexane, the average yield of impure butylbenzene from several runs being about 17–18 per cent. The method used by Stratford,[47] who claimed a 30–32 per cent. yield using bromobenzene and butyl bromide, is far more satisfactory. Similar yields were obtained in our experiments. The hydrocarbon was purified by continued refluxing over sodium and refractionation.

The sample of "Mixed Xylenes" was obtained from the Gas Light and Coke Company. The mesitylene was obtained from Professor Nash, and we are indebted to him for allowing us to include the data in this series.

TABLE VI.

Properties of Cyclohexane Hydrocarbons.

Hydrocarbon.	Cyclo-hexane.	Methyl cyclo-hexane.	Ethyl cyclo-hexane.	o-Dimethyl cyclo-hexane.	m-Dimethyl cyclo-hexane.	p-Dimethyl cyclo-hexane.	n-Propyl cyclo-hexane.	n-Butyl cyclo-hexane.
Boiling Pt. (corrd.) ..	80·9 ±0·1	101·0 ±0·5	131·6	127·9 ±1	121·6 ±1	121·7 ±1	155·7	180·5 ±0·5
$d\ \frac{15}{4}$	0·7820	0·7736	0·7914	0·7912	0·7761	0·7767	0·7968	0·8037
$d\ \frac{20}{4}$	0·7775	0·7696	0·7875	0·7874	0·7723	0·7727	0·7929	0·8005
$n\ \frac{20}{D}$	1·4254	1·4239	1·4320	1·4314	1·4255	1·4253	1·4360	1·4410
Aniline Point	30·2	39·5	43·8	48·3	47·8	47·8	49·8	54·4
Freezing Point	4·5° C.	—	—	—	Below—75° C.	—59° C.	—	—

TABLE VII.

Properties of Aromatic Hydrocarbons.

Hydrocarbon.	Benzene.	Toluene.	Ethyl-benzene.	Mixed Xylenes.	n-Propyl-benzene.	Mesitylene.	n-Butyl-benzene.
Boiling Pt. (corrd.)	80·4	110·4 ±0·2	136·1 ±0·5	138·9 ±0·5	158·6 ±0·7	164·0 ±0·4	182·1–183·1
$d\ \frac{15}{4}$	0·8826	0·8693	0·8722	0·8632	0·8666	0·8708	0·8708
$d\ \frac{20}{4}$	0·8784	0·8652	0·8678	0·8592	0·8628	0·8667	0·8668
$n\ \frac{20}{D}$	1·4995	1·4947	1·4958	1·4920	1·4919	—	1·4880
Aniline Point	Below —30°C.	Below —30° C.	Below —30° C.	Below —30° C.	Below —30° C.	Below —30° C.	Below —30° C.
Freezing Point	5·45°	—	—	—	—	—	—

Experimental Details. Procedure employed in the Engine Tests.

On account of the limited quantity of most of the hydrocarbons which was available, the determination of the engine behaviour of the pure substances was obviously out of the question, and in some cases also, the hydrocarbon would knock either far too heavily, or not at all, in the test-engine employed.

Consequently the measurements were made on a 20 per cent. by volume solution of the compound in the reference fuel known as "Standard Reference Fuel A2," the characteristics of which are given below :—

Table VIII.

Standard Reference Fuel A-2.

Specific Gravity at 60° F.	0·7400
Initial Boiling Point	47° C.
% over at 70° C.	7
,, 100° C.	27½
,, 120° C.	47½
,, 150° C.	77
End Point	197° C.
Octane No. at 212° F.	50·0
,, ,, +1 ml. TEL/Imp. gal .	60·5
Octane No. at 300° F.	47·0
,, ,, +1 ml. TEL/Imp. gal.	57·5

The Octane Number of "A2" being 50·0 at 212° F. jacket temperature, all the 20 per cent. volume solutions of the hydrocarbons in this fuel have octane numbers falling conveniently within the range of the engine.

The engine employed for these measurements was the Ethyl Gasoline Corporation Series 30 model. Its design and operation are well known and have been previously described in the literature.[50] Tests were made at 212° F. and 300° F. jacket temperatures, the precise operating conditions being as shown in Table IX.

Table IX.

Operating Conditions for the S.30. Engine.

Jacket Temperature ..	212° F.	300° F.
Cooling Medium	Water.	Ethylene Glycol Solution.
Compression Pressure ..	195 ± 5 lb. gauge.	195 ± 5 lb. gauge.
Spark Advance	22° before T.D.C.	15° before T.D.C.
Speed, r.p.m.	600.	600.
Air-Fuel ratio	For maximum knock.	For maximum knock.
Indicator	Bouncing-Pin and Knockmeter.	Bouncing-Pin and Knockmeter.

The same engine and operating conditions were used in the investigation on the knock ratings of the α-olefines recently published by Garner, Wilkinson and Nash[1] so that these results are strictly comparable with those recorded in the present paper. In the earlier work recorded by Howes and Nash[29] the older type

of Delco test-engine was employed, the speed being 500 r.p.m. and the jacket temperature about 180° F. The results on the two types of engines do not, however, differ very greatly.

Four measurements were carried out, wherever possible, on the 20 per cent. volume solution of each of the cyclic hydrocarbons in "A2"; that is the octane numbers of the blend were determined at jacket temperatures of 212° F. and 300° F., both with and without the addition of one ml. of lead tetraethyl per imperial gallon. To carry out these four determinations on the S.30 engine, a minimum quantity of about 500 ml. of the 20 per cent. blend was required.

The error in the determination of the octane number of the 20 per cent. solutions appears to be about $\pm$ 0·5 octane number.

Experimental Results and Discussion.

Treatment of experimental data.—The octane numbers of the 20 per cent. volume solutions at 212° F. and 300° F. jacket temperatures are given in Tables X. and IX. in the first column. In the cases of the series of ring compounds with one substituent group, the results of these determinations, plotted against the numbers of carbon atoms in the compounds, give regular curves within the limits of experimental error. The values read off from these curves give the "smoothed values" in the second columns of the tables. Tables XII. and XIII. give similar values of the results for the aromatic hydrocarbons published by Howes and Nash,[31] and for the α-olefines recorded by Garner, Wilkinson and Nash.[1] In the case of Howes and Nash's results the values have been converted to octane numbers from the form in which they were originally given. The values of 20 per cent. volume solutions in "A2" were then calculated from the values in "A.M.B." by a method described by Garner, Wilkinson and Nash. The values for the α-olefines have also been converted from reference fuel "A.M.B." (Octane Number 52) to reference fuel "A2" (Octane Number 50). The previous knock rating determinations on several branched chain aromatics are included here, together with the results on the complete series of straight chain derivatives from benzene to n-butylbenzene obtained in the present experimental work. Data on some fifteen aromatic hydrocarbons are therefore now available, and as all these boil in the range 80° C. to 183° C., a fairly complete picture can be drawn of the behaviour of the aromatic hydrocarbons present in gasoline.

The α-olefines form the only other series of hydrocarbons for which knock rating determinations are available in the octane-heptane scale and are interesting for purposes of comparison with the new data presented here.

From the "smoothed values" of the 20 per cent. volume solutions, the "blending octane numbers" of the hydrocarbons can be calculated on the assumption that a straight-line mixture relationship holds for blends of hydrocarbons and reference fuel, i.e.:

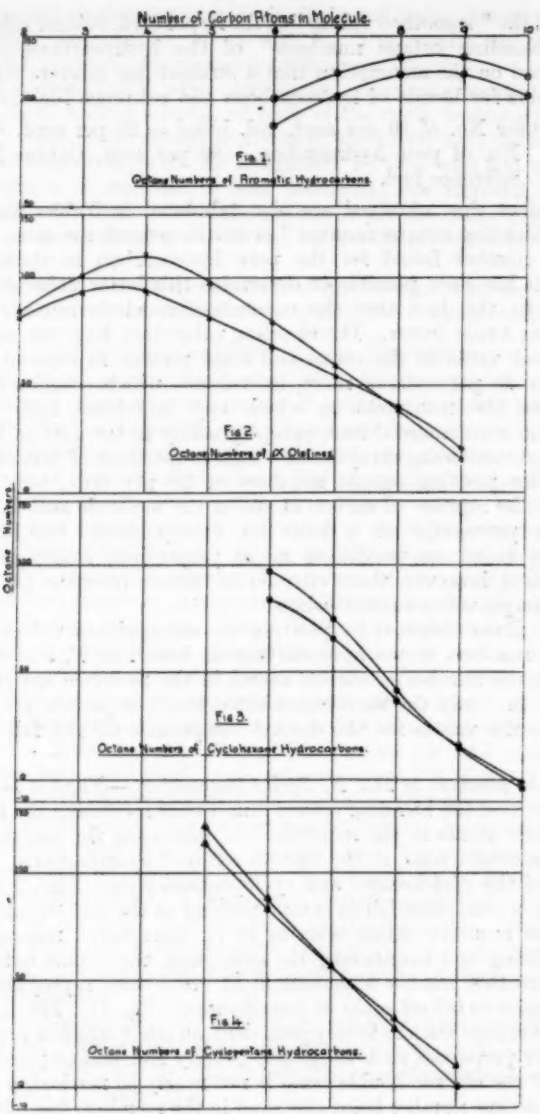
> Octane No. of 20 per cent. vol. blend = 20 per cent. Octane No. of pure hydrocarbon + 80 per cent. Octane No. of reference fuel.

The values thus obtained are also tabulated in Tables X.–XIII. The "blending octane number" is not in general the same as the octane number found for the pure hydrocarbon in those cases where it has been possible to determine this latter value directly, owing to the fact that the concentration-octane number curve is not, as a rule, linear. The blending value does, however, measure the knock value of the compound when present in concentrations of up to 20 per cent. or more, by volume, which concentration is probably the maximum in which any individual hydrocarbon occurs in a commercial fuel, except possibly in the case of benzole mixtures containing exceptionally high proportions of benzene.

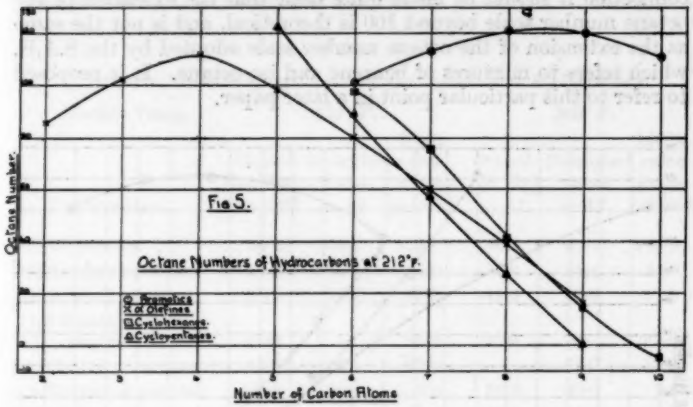
Besides plotting octane numbers of 20 per cent. vol. blends against the number of carbon atoms in the molecule and using the volume percentage as a basis for extrapolation, various other systems based on weight or molar proportions might be used. In general, however, these offer no advantage over the use of the more simple volume relationships.

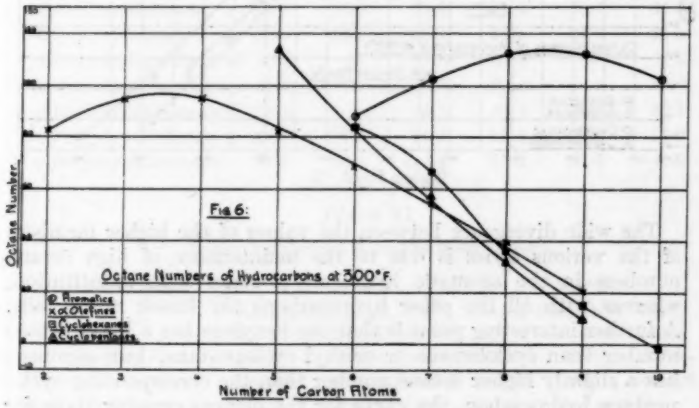
The curves obtained by plotting the extrapolated values of the octane numbers of the hydrocarbons at both 212° F. and 300° F., against the number of carbon atoms in the molecule are given in Figs. 1–6. Only the mono-substituted ring compounds are shown here as the values for the dialkyl compounds do not fall on the curves.

Octane numbers at 212° F. Jacket temperature.—Figures 1–4 show the effect on the blending octane numbers of increasing the number of carbon atoms in the molecule, i.e., increasing the length of the paraffinic side-chain, in the various series of hydrocarbons. In the cases of the cyclohexane and cyclopentane series (Figs. 3 and 4), there is a consistent fall in octane number as the series is ascended, but the aromatic series behaves in an unexpected manner. On introducing and lengthening the side-chain, the octane number at first increases, reaches a maximum at ethyl- and n-propylbenzene and begins to fall off again at butylbenzene (Fig. 1). The influence of the benzene nucleus is very persistent, an effect which is noticeable in other properties such as specific gravity and aniline point, while that of the olefinic double bond is not nearly so marked, a regular fall in octane number being observed in the members from butene-1


Number of Carbon Atoms in Molecule.
Fig 1.
Octane Numbers of Aromatic Hydrocarbons.
Fig 2.
Octane Numbers of α Olefines.
Octane Numbers.
Fig 3.
Octane Numbers of Cyclohexane Hydrocarbons.
Fig 4.
Octane Numbers of Cyclopentane Hydrocarbons.

onwards. An interesting point is the slight, but quite definite, double bend in the cyclohexane series at the second member of the series. Cyclohexane differs very little in its blending effect in

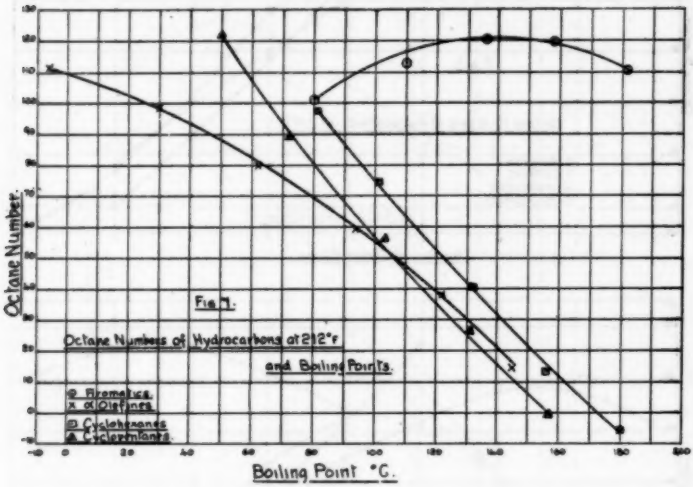




20 per cent. concentration from pure benzene in the same concentration, although pure cyclohexane can readily be made to knock, whereas Boyd has subjected pure benzene to a compression ratio of 15:1 without knocking occurring.

In Fig. 5 is given a comparison of the blending values at 212° F. of the various series of hydrocarbons plotted against the number of carbon atoms in the molecule. It will be noted that hydrocarbons

containing 6 carbon atoms show a range of only 20 octane numbers between the different series, whereas the hydrocarbons containing 9 carbon atoms have a maximum difference of over 100. In this connection it should be made quite clear that the extension of the octane number scale beyond 100 is theoretical, and is not the same as the extension of the octane number scale adopted by the S.A.E. which refers to mixtures of benzene and iso-octane. It is proposed to refer to this particular point in a later paper.



The wide divergence between the values of the higher members of the various series is due to the maintenance of high octane numbers in the aromatic hydrocarbon series with substitution, whereas with all the other hydrocarbons the knock rating falls. A further interesting point is that the hexylene has a lower octane number than cyclohexane or methyl cyclopentane, but α-nonene has a slightly higher octane number than the corresponding cyclopentane hydrocarbon, the curve for the olefines crossing those for the two saturated cyclic hydrocarbon series. Fig. 7 gives similar data in reference to the connection between octane number and boiling point, and thus is, perhaps, of more direct practical importance than the previous curve relating to the number of carbon atoms in the molecule. The general tendency of the curve is, however, precisely similar, and shows that for the various series of hydrocarbons the ascending order at 80° C. boiling point is

olefine, cyclopentane, cyclohexane, aromatic; at 100° C., is the same; and at 150° C. the olefine and cyclopentane are approximately equal, but the difference between these hydrocarbons and the aromatic hydrocarbons is very great.

TABLE X.

Octane Numbers of Cyclopentane and Cyclohexane Hydrocarbons.

Jacket Temp.	212° F.			300° F.		
Hydrocarbon.	Octane No. 20% in A2.	Smoothed value in A2.	100% value. extrapolated.	Octane No. 20% in A2.	Smoothed value in A2.	100% value. extrapolated.
Cyclopentane.. ..	64·2	64·4	122·0	60·4	60·4	114·0
Methylcyclopentane ..	57·8	57·8	89·0	54·0	54·4	84·0
Ethylcyclopentane ..	51·3	51·4	57·0	49·5	49·0	57·0
1-3-Dimethylcyclopentane ..	57·0	—	85·0	55·0	—	87·0
n-Propylcyclopentane	45·0	45·4	27·0	—	44·0	32·0
n-Butylcyclopentane ..	40·0	40·0	0·0	39·5	39·5	9·5
Cyclohexane	59·1	59·5	97·5	53·8	54·4	84·0
Methylcyclohexane ..	55·7	55·0	75·0	51·5	50·7	65·5
Ethylcyclohexane ..	48·0	48·2	41·0	44·0	44·7	35·5
o-Dimethylcyclohexane	56·2	—	81·0	51·8	—	71·0
m-Dimethylcyclohexane	53·7	—	68·5	51·5	—	69·5
p-Dimethylcyclohexane	54·7	—	73·5	50·1	—	62·5
n-Propylcyclohexane ..	42·7	42·8	14·0	41·0	40·6	15·0
n-Butylcyclohexane ..	39·0	39·0	—5·0	37·2	37·2	—2·0

TABLE XI.

Octane Numbers of Aromatic Hydrocarbons.

Jacket Temp.	212° F.			300° F.		
Hydrocarbon.	Octane No. 20% soln. in A2.	Smoothed value of 20% soln.	100% value extrapolated.	Octane No. of 20% soln. in A2.	Smoothed value of 20% soln.	100% value extrapolated.
Benzene	60·2	60·2	101·0	55·2	55·2	88·0
Toluene	62·2	62·6	113·0	58·0	58·0	102·0
Ethylbenzene ..	64·1	64·1	120·5	60·0	60·0	112·0
Mixed Xylenes ..	62·5	—	112·5	56·1	—	92·5
n-Propylbenzene ..	64·0	64·0	120·0	59·9	60·0	112·0
Mesitylene	66·2	—	131·0	64·4	—	134·0
n-Butylbenzene ..	62·1	62·1	110·5	56·8	58·0	102·0

TABLE XII.

Aromatic Hydrocarbons (from results of Howes and Nash[31]).

Hydrocarbon.	212° F. Octane No. 20% soln. in A2.	100% value extrapolated.
Benzene	59·2	96·0
Toluene	61·3	106·5
Ethylbenzene	64·6	123·0
o-Xylene	62·8	114·0
m-Xylene	65·1	125·5
p-Xylene	65·6	128·0
iso-Propylbenzene	60·9	104·5
p-Cymene	65·6	128·0
sec-Butylbenzene	58·2	91·0
tert-Butylbenzene	62·8	114·0
tert-Amylbenzene	62·8	114·0
p-tert-Butyltoluene ..	64·6	123·0

TABLE XIII.

Octane Numbers of α-Olefines.

Jacket Temp.	212° F.			300° F.		
Hydrocarbon.	Octane No. of 20% vol. soln. in A2.	Smoothed value in A2.	100% value extrapolated.	Octane No. of 20% vol. soln. in A2.	Smoothed value in A2.	100% value extrapolated.
Ethylene	57·3	57·1	85·5	54·1	54·1	82·5
Propylene	60·0	60·4	102·0	56·4	56·5	94·5
Butene-1	62·8	62·3	111·5	56·6	56·6	95·0
Pentene-1	59·8	59·7	98·5	53·4	54·0	82·0
Hexene-1	54·7	56·0	80·0	51·2	51·3	68·5
Heptene-1	51·9	51·9	59·5	48·8	48·5	54·5
Octene-1	48·4	47·7	38·5	46·2	45·5	39·5
Nonene-1	42·4	43·0	15·0	39·2	41·6	20·0

The above remarks and curves apply only to the hydrocarbons in which normal alkyl radicles have been substituted as the results for the various di- or iso- substituted benzene, cyclohexane and cyclopentane hydrocarbons do not fall on smooth curves.

Lovell, Campbell and Boyd[36] showed that in general, the more centralised the molecule the greater the octane number, in so far as the paraffin and olefine series of hydrocarbons was concerned, and this general rule would appear to hold both for the aromatic and the two naphthene series of hydrocarbons. Thus, methyl-cyclopentane, 1-3-dimethyl-cyclopentane and ethyl-cyclopentane

have blending octane numbers of 89, 81 and 57 respectively, Similar tendencies are observed with the three dimethyl-cyclohexanes.

Howes and Nash[31] have already commented fully on the results obtained for the aromatic hydrocarbon series. They state that in general the substituted benzenes are the best anti-knocks, and tertiary groupings appear to have a better effect than secondary groupings. The problem as regards aromatic hydrocarbons is complicated by reason of the fact that we have three separate influences to consider: (1) the effect of the benzene nucleus; (2) the effect of the position of the substituent, i.e., whether ortho, meta or para; and (3) the constitution of the hydrocarbon radicle combined with the benzene nucleus. Thus it is not possible to reach any very definite relationship as regards the substituted aromatic hydrocarbons, but the following table shows the effect of isomerism in the aromatic series. In view of relatively slight differences in octane numbers of 20 per cent. solutions of aromatic hydrocarbons, it would obviously be undesirable to stress too greatly the difference between the octane numbers of the various aromatic hydrocarbons.

TABLE XIV.

The Effect of Isomerism in the Aromatic Series.

No. of Carbon Atoms.	9.	10.	11.
Normal	120·0	110·5	—
Iso	104·5	—	—
Secondary	—	91·0	—
Tertiary	—	114·0	114·0
p-Methyl-iso	—	128·0	—
p-Methyl-tert	—	—	123·0
1-3-5-Trimethyl	131·0	—	—

One very interesting result is the high knock rating obtained for mesitylene which appears to have the highest octane number of any hydrocarbon yet prepared.

Our knowledge of the proportions of cyclohexane and cyclopentane hydrocarbons present in gasoline is, as has already been pointed out, relatively limited, but the octane numbers of the two series run very close together and sixty would appear to be a fair average value of those occurring in gasoline. The octane numbers of the aromatics lie in a very narrow range and 114 is probably an excellent average value.

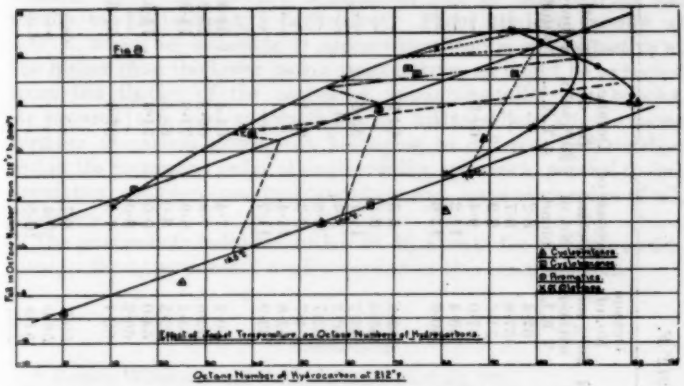
Octane numbers at 300° F. jacket temperature.—Tables X., XI. and XIII., and Figs. 1, 2, 3, 4 and 6 give the results at 300° F. jacket temperature. These figures were treated as in the case of the knock ratings at 212° F., the smooth values for the 20 per cent.

blends being obtained where possible and used for extrapolation. The octane number of the reference fuel "A2" is 50 at 212° F., and 47 at 300° F. jacket temperature. In all cases there is a drop in octane number of the 20 per cent. solutions at 300° F. jacket temperature as compared with the octane numbers at 212° F. The curves for the blending value of the pure hydrocarbons show an interesting change as the number of the carbon atoms increases. The curves representing octane numbers at 212° F. and 300° F. for cyclopentane, cyclohexane and the olefine hydrocarbons (Figs. 2, 3 and 4) in each case cross near the point representing the hydrocarbon containing eight carbon atoms. Thus, whilst with the lower members the octane number at 212° F. is higher than at 300° F., the reverse holds with the higher members of all these series and the octane number is actually greater at 300° F. than at 212° F. jacket temperature.

For the normal alkylated aromatic hydrocarbon series (see Fig. 1) in every case the octane number at 212° F. is greater than that at 300° F. jacket temperature. It was, however, found that in the case of mesitylene that the octane number at 300° F. was apparently higher. Unfortunately, little information as regards aromatic hydrocarbons other than normal alkylated aromatic hydrocarbons is available at the higher jacket temperature. A point of interest in this connection is, however, the high octane number and the relative insensitiveness of dimethyl-cyclopentane to jacket temperature (blending octane value at 212° F.–85, at 300° F.–87). This is rather surprising in view of the fact recorded by Chavanne,[12] that this hydrocarbon is spontaneously oxidised in air, iso-amyl acetate and methyl iso-amylacetone being formed through peroxidation. m-Dimethyl cyclohexane has a higher blending octane value at 300° F. than 212° F., but the o- and p-hydrocarbons are similar to the lower cyclohexane hydrocarbons. In general (see Figs. 5 and 6), it may be stated that the *relative* order of the octane numbers of the various types of hydrocarbons is the same at 300° F. as at 212° F.

In Fig. 8 is shown the octane number difference on increasing the jacket temperature from 212° F. to 300° F., plotted against the octane number for the hydrocarbon at 212° F. jacket temperature. This curve is of special interest as it shows that there is a definite tendency in each series for the fall in octane number at the higher jacket temperature to become less the lower the octane number. A point of some importance when comparisons of octane numbers at two jacket temperatures are made, is that the effect of the temperature on the two reference hydrocarbons—iso-octane and heptane—must be taken into account, and this point also will be further discussed in a later paper.

Fig. 8 shows that it is possible with aromatic hydrocarbons to have two hydrocarbons of the same octane number with different falls in octane number from 212° F. to 300° F. Three series of lines connect points of equal boiling points in the different series of hydrocarbons. These show clearly that for equal boiling points, the temperature susceptibilities of the hydrocarbons are in the order, cyclopentanes, cyclohexanes, α-olefines and aromatics, the last series showing by far the greatest drop in octane number on raising the jacket temperature. It is to be expected, therefore, that fuels


Fall in Octane Number from 212° to 300°F.
Effect of Jacket Temperature on Octane Numbers of Hydrocarbons.
Octane Number of Hydrocarbon at 212°F.

owing their anti-knock properties to the presence of olefines, such as cracked fuels, or to the addition of benzole, will not be so satisfactory at the higher temperatures as fuels composed mainly of paraffins and naphthenes. This is more particularly applicable to fuels for use in aircraft engines, the conditions for which are duplicated more closely by the knock rating at the higher jacket temperature.

Lead susceptibility.—The final series of measurements deals with the effect of adding lead tetraethyl in the proportion of one ml. per imperial gallon to the 20 per cent. by volume blend of the hydrocarbons. The results obtained are given in Table XV., which shows the increase in octane number of the 20 per cent. volume blends on adding lead tetraethyl. Wherever possible, smoothed values are employed to calculate the increases in octane number.

Lead susceptibilities of all the hydrocarbons have been determined at 212° F. jacket temperature, but in consequence, partly of lack of material and partly of the way in which the investigation has developed over a considerable period of time, only nine measurements were obtained at 300° F.

TABLE XV.—LEAD SUSCEPTIBILITIES OF 20% VOL. SOLUTIONS OF HYDROCARBONS.

Jacket temperature.	212° F.				300° F.			
Hydrocarbon.	Octane No. of 20% soln. + T.E.L.	Smoothed value of same.	Octane No. of 20% soln. without T.E.L.	Increase of Octane No. of blend.	Octane No. of 20% soln. + T.E.L.	Smoothed value of same.	Octane No. of 20% soln. without T.E.L.	Increase of Octane No. of blend.
Cyclopentanes.								
Cyclopentane	72·8	72·6	64·4	8·2	—	—	—	—
Methylcyclopentane	—	66·5	57·8	8·7	—	—	—	—
Ethylcyclopentane	61·3	61·3	51·4	9·9	—	—	—	—
1-3-dimethylcyclopentane	66·4	66·4	57·0	9·4	64·9	—	55·0	9·9
n-Propylcyclopentane	56·8	56·6	45·4	11·2	—	—	—	—
n-Butylcyclopentane	52·6	52·6	40·0	12·6	—	—	—	—
Cyclohexanes.								
Cyclohexane	66·1	66·0	59·5	6·5	64·9	—	54·4	10·5
Methylcylohexane	64·9	64·5	55·0	9·5	—	—	—	—
Ethylcyclohexane	57·8	59·3	48·2	11·1	55·5	—	44·7	10·8
o-Dimethylcyclohexane	64·6	64·6	56·2	8·4	—	—	—	—
m-Dimethylcyclohexane	63·5	63·5	53·7	9·8	—	—	—	—
p-Dimethylcyclohexane	63·0	63·0	54·7	8·3	61·1	—	50·1	11·0
n-Propylcyclohexane	55·4	54·2	42·8	11·4	—	—	—	—
n-Butylcyclohexane	50·0	50·5	39·0	11·5	—	—	—	—
Aromatics.								
Benzene	67·6	67·6	60·2	7·4	64·4	64·4	55·2	9·2
Toluene	70·8	70·4	62·6	7·8	69·2	69·2	58·0	11·2
Ethlybenzene	73·0	73·0	64·1	8·9	71·8	71·8	60·0	11·8
Mixed xylenes	70·5	70·5	62·5	8·0	68·5	—	56·1	12·4
n-Propylbenzene	73·3	73·0	64·0	9·0	71·9	71·9	60·0	11·9
Mesitylene	76·1	76·1	66·2	9·9	—	—	—	—
n-Butylbenzene	68·8	69·4	62·1	7·3	67·6	67·6	58·0	9·6
α-Olefines.								
Pentene-1	68·4	68·4	59·7	8·7	—	—	—	—
Hexene-1	64·5	65·4	56·0	9·4	—	—	—	—
Heptene-1	61·6	62·4	51·9	10·5	—	—	—	—
Octene-1	60·8	59·5	47·7	11·8	—	—	—	—
Nonene-1	55·4	56·5	43·0	13·5	—	—	—	—

It does not seem practicable to treat the rises in octane number due to lead additions as purely additive, and consequently the susceptibility of the hydrocarbon has not been separated from that of the reference fuel. The octane number of the latter is 47 at 300° F. and 57·5 after the addition of one ml. tetraethyl lead per gallon, giving a rise of 10·5 octane numbers.

There is a definite rise of the lead susceptibility at 212° F. in all series, including the α-olefines reported by Garner, Wilkinson and Nash, as the length of the paraffin chain increases, and the octane number falls. No definite conclusions can be drawn from the results on the dimethyl derivatives. From the few results at 300° F. which are available, it appears that lead is more effective at the higher than the lower jacket temperature, as might be expected from the theory of the action of organo-metallic anti-knocks. As regards the lead susceptibility of hydrocarbons of the same number of carbon atoms, but belonging to different hydrocarbon series, the increasing order of susceptibility appears in general to be ; aromatics, cyclohexanes, cyclopentanes and, most responsive of all, α-olefines.

The authors are indebted to Mr. C. H. Sprake for valuable assistance in the experimental work recorded in this investigation.

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Note on the Geology of the Ionian Islands.

By Arthur Wade, D.Sc., A.R.C.Sc., etc. (Member).

1. Introduction.

In describing the geology of Zante in his recent paper, the author felt that he was dealing with a fraction of a geological unit which would be better dealt with as a whole. The subsequent discussion showed that there was need of broader treatment, but lack of knowledge of much of the detailed geology of the Ionian region makes such treatment impossible except on general lines.

Phillippson and Wray recognise two distinct zones in the folded area of Western Greece, the Ionian zone and the zone of Pindus. The zones of the Ægean, to the East, are totally distinct and differ both in constitution and structure. The picture into which we have to fit Zante, therefore, is that of the Ionian zone and not that of the Ægean.

Now the most thorough account of the Ionian Islands is embodied in a remarkable book written by John Davy (brother of Sir Humphrey) nearly one hundred years ago, but though Davy's geological descriptions are shrewd and accurate he concerns himself but little with structure. Phillippson and Wray take a bird's-eye view which, of necessity, is too broad to take in what is merely local. During the past ten or twelve years, however, much geological work has been done in this area by Continental geologists and some by British workers, though little has been made public by the latter. The series of papers published by Carl Renz has thrown a good deal of light on the geology of the Ionian zone. Not only has he mapped Ithaka in detail, but he has contributed largely to geological and palæontological knowledge of S. Maura and other parts of the western coasts of Greece. The Italian geologists, Stefani and Martelli, have also published accounts of investigations made in S. Maura (Leuca) and the islands of Paxos and Antipaxos.

The author, therefore, has based this note on information gained from the works of those mentioned above, from the section of the Carte Internationale Géologique which includes the Ionian region, and from personal observations made on several of the islands of the Ionian archipelago.

2. The Structure of the Ionian Islands.

Structurally the Ionian Islands are part of a belt of folded Cretaceous-Eocene limestones which trends almost due S.E. from Corfu and the neighbouring coast to the Gulf of Arta, and from

thence swings round forming an arc which terminates in Zante, where the S.E. trend is taken up again. A continuation of this belt is represented in a narrow coastal strip forming the extreme S.W. corner of the mainland of Greece.

There is some evidence to show that the break in the line in the neighbourhood of the Gulf of Arta and the termination of the Ionian group to the S. of Zante are due to E. and W. faults parallel to the great faults of the Gulf of Corinth. It may be noted that earthquakes are more prevalent in the islands S. of the Gulf of Arta (with the exception of Ithaka) than in those to the N. Also, in spite of statements made in some recent works of reference,* there are no igneous rocks nor evidences of volcanic activity anywhere in this zone.

This folded limestone belt pitches both to N.W. and S.E. Thus on Corfu to the N.W. the limestones form no large part of the surface which is mostly occupied by deposits of later age, while on Zante, to the S.E., deposits of Miocene and of more recent age occupy a proportionately larger surface area than on any of the remaining islands. The limestones reach their maximum development at the surface and elevation above sea level in the region of Cephalonia, where they rise to heights of over 5000 ft. above the sea. Here they form three distinct and parallel belts of rugged hill country, two of which are on Cephalonia and the third on the neighbouring island of Ithaka. Structurally these limestone belts of Cephalonia and Ithaka consist of two parallel anticlinal folds separated by a synclinal depression occupied by deposits ranging upwards from the Miocene. The peninsula of western Cephalonia is the crest of the unbroken western fold, an asymmetrical anticline, striking almost due N. and S. with the steeper dip to the E., and in which the limestone mountains do not attain such elevation above sea-level as they do in the Black Mountain of central Cephalonia. This fold is the obvious prolongation of the similar fold of western Zante. The crest of this outer anticline disappears beneath the waters of the Ionian sea N. of Cephalonia, but comes up again in the islands of Paxos and Antipaxos, and constitutes the geological foundation of Corfu. In Paxos and Antipaxos the nature of the folding is unchanged, the structural similarity causing these two islands to resemble strongly the mountain region of Zante.

The limestone belts of central Cephalonia and Ithaka are part of one broad, broken anticline, and attain considerable elevation above sea-level. In the broken crest of this fold not only is the

* Encyclopædia Britannica, 14th edition, vol. 23, p. 934: ". . . other volcanic indications are the oil springs . . ." Mediterranean Pilot (British Admiralty), vol III., pp. 45–50: "Traces of volcanic agency are visible in many parts of the island."

base of the limestone group exposed, but underlying strata of Jurassic age as far down as the "Dogger" have been recognised and described by Renz, the classification being well supported by palæontological evidence. The two limbs of this broken crest pass northwards from Cephalonia and Ithaka into S. Maura, where Jurassic fossils have also been discovered and described by both Davy and Renz. They merge in the northern part S. Maura, and pass on to the mainland. This great broken fold disappears to the southward of Cephalonia and Ithaka, but the anomalous south-eastern peninsula of Zante is in line with a continuation of the strike of the central limestone belt of Cephalonia. The limestones of Mt. Skopos, which the author, in his earlier paper, has assigned to the Cretaceous-Eocene group with which we are dealing, thus fall into place in any general structural consideration of the islands.

The marls, clays, gypsums and sandstones occupying the central depression of Zante are found again in the synclinal trough of Cephalonia, which is a continuation of it, the break between being merely a topographical accident. It will be found, when further research is accomplished, that the structural geology of Cephalonia and Ithaka cannot be well understood without reference to Zante, the converse being, in all probability, equally true. Though the tectonic features thus dealt with are not quite so simple as we have assumed, they hold good for any general account of this area. It may be noted that we have, as yet, no evidence of overfolding in the remaining islands such as that described by the author in the uplift of Mt. Skopos, of which Davy says (3, vol. 1, p. 79) that it looks as if very recently formed, probably by volcanic or analagous forces, and compares the highly tilted strata with the almost horizontal beds a little to the N. North of the Ionian area, however, in the neighbourhood of Yanina in Western Greece (Epirus) and near Dulcigno in the extreme S. of Jugo-Slavia, Georgalas, Wray and Zuber (9 sections facing p. 6) have described similar structures in strata of the same age and nature. In the country near Yanina strata of Lower Tertiary age are thrust over Miocene deposits as in Zante (2.21).

3. The Junction between the Cretaceous and the Eocene in the Ionian Zone.

The important limestone group which is the main feature of the Ionian zone presents for solution problems of its own. In places it is a mass of Nummulites and is, therefore, of Eocene age. Below the Nummulitic beds, massive strata of grey or dark limestones occur which are often practically devoid of distinguishable fossils. In other places the underlying limestones contain Rudistids in

large numbers, species of Hippurites being especially abundant. These fossils clearly indicate that these underlying beds belong to the Cretaceous. This apparent passage of strata of Cretaceous age upwards into the Eocene, which was noted in the paper on Zante, evoked some comment, but the difficulty of finding a definite break between the two formations is not confined to Zante, it has been experienced throughout the Ionian group. The geological cartographers responsible for the Carte Internationale Géologique found it convenient to map the Cretaceous and Eocene together as one formation in their map of this region. Renz found it impossible to draw the line between them in his detailed geological map of Ithaka, while other geologists who have worked in this region have met with the same difficulty not only on other islands of this archipelago but also on the islands of the Italian Dodecanese. As is so frequently the case where difficulties of this kind exist, the solution of the problem may be found by a study of these Cretaceous-Eocene limestones in neighbouring territory sufficiently near to the Ionian area for the deposits to be similar in character and directly traceable from one area to the other, but sufficiently distant for slight differences to have occurred in conditions of deposition. Thus, to the North, in Albania, into which the Ionian zone passes and in the old kingdom of Montenegro in southern Jugo-Slavia, a distinct break can be established, not always without difficulty, between the limestones with Hippurites (Cretaceous) and the Nummulitic limestones (Eocene) owing to the presence of bauxite, which occurs in irregular patches between the two formations. Zuber's description of the succession in this region is as follows [9, p. 17] :—

" 1. Calcaire à Rudistes.

2. Calcaires blancs de l'Éocène a l'épaisseur environs 50–150 mètres. Entre ces calcaires et la série précédente existe une lacune bien caractéristique grâce à la présence des amas de bauxite."

The two following quotations from Desio's recent work not only indicate the nature of the passage from Cretaceous to Eocene in the islands of the Dodecanese, but show how close a parallel there is in the sequence in these two areas :—

" Una successione regolare che lasci vedere con chiarezza il passagio dalla Creta all' Eocene non è nota in alcuna della isole del Dodecaneso, salvo a Rodi, ove sui gruppi dell' Attairo e dell' Acramiti-Armenisti, si passa regolarmente dai calcari grigi compatti, più o meno breccioidi e selciferi con Orbitoline e piccoli resti di Hippuriti, a calcari breccioidi con Orbitelle e pure con frammenti di Hippurite, a calcari selciferi, ben stratificati con Nummuliti. *Sembra si tratti di una facies molto simile a quella adriatico-ionia* " [13, p. 425].

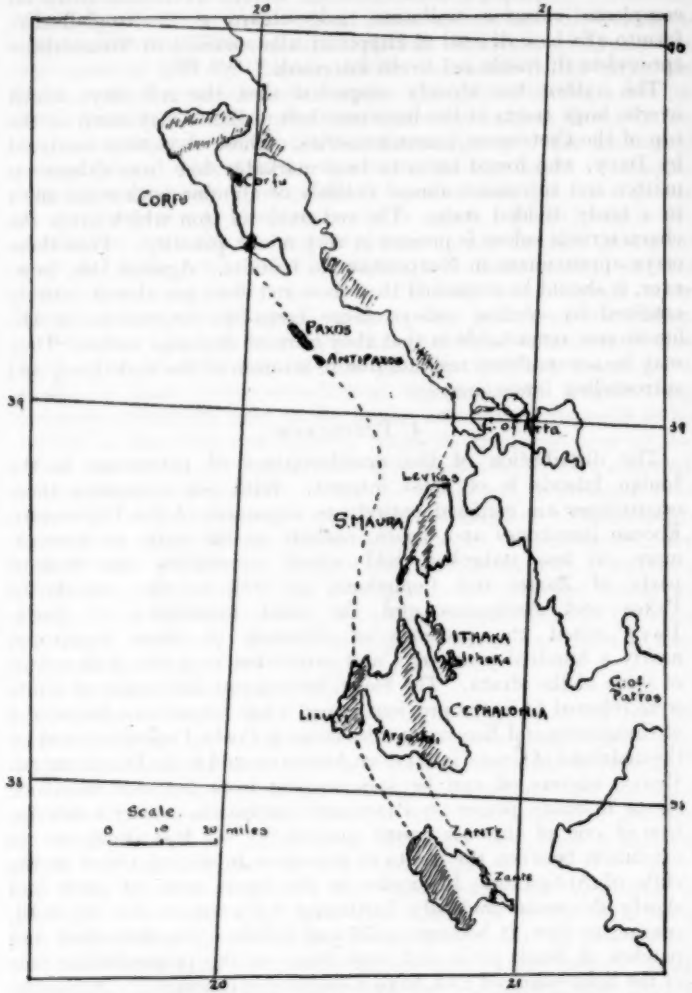
Also : " Il passagio della Creta all' Eocene avverebbe entro un complesso calcareo uniforme, grigo-chiaro e bianco-giallastro, fornito alla base di resti di Hippuriti, alla sommità di Nummuliti e sprovvisto di fossile nei livelli intermedi " (13, p. 426).

The author has already suspected that the red clays which overlie large tracts of the limestone belt of Zante may occur at the top of the Cretaceous limestone series. These clays were analysed by Davy, who found them to be remarkably free from calcareous matter and to consist almost entirely of alumina with some silica in a finely divided state. The red oxide of iron which gives the characteristic colour is present in very minor quantity. Thus these clays approximate in composition to bauxite. Against this, however, it should be remarked that these red clays are almost entirely confined to solution valleys, large basin-like depressions in the limestones, remarkable in that they have no drainage outlet. They may be accumulated residues due to solution of the underlying and surrounding limestones.

4. Petroleum.

The distribution of the manifestations of petroleum in the Ionian Islands is of great interest. With one exception these occurrences are confined entirely to exposures of the Cretaceous-Eocene limestones and, again, entirely to the outer or western, more or less unbroken fold which constitutes the western parts of Zante and Cephalonia as well as the islands of Paxos and Antipaxos and the solid foundation of Corfu. Davy noted the presence of bitumen in these limestones nearly a hundred years ago, and attributed to it the dark colour of some of the strata. The black, bituminous limestones of Zante were referred to in the previous paper, while bituminous limestones of Cretaceous and Eocene age also occur in Corfu, Cephalonia and on the mainland of Greece in Western Acarnania and in the Peloponnesus. Heavy viscous oil can be seen seeping from between limestone strata in many places on Paxos and Antipaxos. Davy's description of one of these is worth quoting (3, p. 88). " It occurs as an exudation between the strata of limestone in several places in the cliffs of Antipaxos. It exudes in the liquid state of pitch and slowly descends gradually hardening by exposure to air until, ceasing to flow, it becomes solid and brittle. The dark lines and patches of black pitch and asphaltum on the perpendicular face of the light coloured rock have a singular appearance." According to Wray these limestones have an average content of 14 per cent. of asphalt.

Near where the limestones run out to sea to the S. of Zante heavy petroleum can be seen on still days bubbling up from the



STRUCTURAL TRENDLINES AND DISTRIBUTION OF CRETACEOUS-EOCENE LIMESTONES (SHADED) IN THE IONIAN ISLANDS.

sea floor at the base of the cliffs, and on such days it is an easy matter to collect samples. Davy notes a similar oil spring in the sea between Keri Point on Zante and the island of Marathonisi, about three miles from Keri Bay.

It has already been noted that a continuation of the Ionian zone is to be found in the south-western corner of Greece. The limestones form a coastal belt in the neighbourhood of Marathopolis and Modon (anc. Mothone or Methone), where seepages of heavy oil have been known since ancient times. Of this occurrence (Modon) Pausanias (14, Bk. IV., ch. xxxv.) says: "There is also a sanctuary of Artemis here and a well of water mixed with pitch; in appearance the water is very like the fragrant oil of Cyzicus." Wray says that the Nummulitic limestones of Marathos or Marathopolis contain bands uniformly impregnated with asphalt, the mean yield ranging between 7 and 8 per cent.

The one exception referred to above is the seepages at and near to the Herodotus well on Zante, which have already been described and which are from Miocene strata forming a comparatively shallow covering over the Cretaceous-Eocene limestones. Davy's book, which is remarkable both for originality and acumen, must contain one of the earliest suggestions that oil could be obtained in commercial quantities by the drilling of wells, a suggestion made after he had examined the area around the ancient well on Zante, as well as some speculations as to the origin of oil (which he concludes must have been formed, like coal, from vegetable matter), which appear to have been overlooked by writers on this subject though they are well worthy of attention.

5. Conclusion.

In this brief contribution to the geology of the Ionian region the author has attempted to sketch in the fundamental structural picture as a whole, to show the various members of the Ionian archipelago in their geological relationships to each other and, incidentally, to connect the work done on Zante with geological researches carried out elsewhere in these islands, and so remove misapprehensions which may be caused by considering Zante alone instead of as but a small part of a larger geological unit.

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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

RUMANIAN BRANCH.

THE THIRTY-FOURTH GENERAL MEETING of the Rumanian Branch of the Institution of Petroleum Technologists was held at the Chamber of Commerce, Ploesti, on December 18th, 1931, Capt. Treacy, Chairman, occupying the Chair.

The following paper was read by the author :—

Production after Gas Lift.

By L. W. ROGERS.

The production of an oil well after completion usually commences with a flowing period, to be followed, when the well no longer has sufficient energy to produce itself, by the mechanically lifted period. This second stage offers great scope for the far sighted vision and study of the production engineer, in order that the potential production of the well will be obtained in the most economical manner possible, and with the smallest investment of capital. For the full mechanical period there are the following alternatives available as regards production systems :—

Gas-lift.
- 1. (*a*) Individual well pumping installations.
  (*b*) Bailing or Swabbing.
  } Pumping powers.
- *Or*
- 2. Some system using compressed gas as the medium for lifting oil.

There seems little doubt that the mechanical stage after flowing will continue in the future to commence with gas lifting. Improvements over present methods will be mainly concerned with a greater knowledge of the most efficient tubing sizes for certain conditions and with compressor design. When a gas lift period is anticipated it becomes necessary to make a considerable investment for compressors and the whole gas lift installation which includes : output gas manifold and connection to each well ; and gas gathering system between wells, compressor house and absorption plant ; in all a large amount of machinery and network of gas lines which represent a very large outlay of capital for transport and installation alone.

Alternative 1.—The installation of individual well pumping units after gas lift (bailing and swabbing being left out of consideration) makes compressors in their present location no longer necessary The whole gas lift installation must be moved to another location

or, what is more likely to be the case, it will remain idle and the length of time for the amortisation of equipment will be lengthened. Absorption plants will immediately feel a shortage of gas as soon as gas lifting ceases. Additional equipment for individual well pumping installations must be purchased in good time, so that pumping can be applied as soon as gas lifting is no longer economical. At a later stage, and particularly when wells do not require to be pumped continuously for 24 hours a day, it is often found to be more economical to install a pumping power for a group of wells. This latter practice is limited by the depths of the wells and the surface contour.

Alternative 2—which is the application, immediately after gas lift, of a system by which oil is lifted with compressed gas—has the great advantage that the whole gas lift installation will continue to be used in its present location for the remaining life of the wells. The number of compressor units employed can be held in proportion to the gradually declining input gas demands. There is the further advantage that input gas used for lifting oil can be re-cycled to an absorption plant for gasoline extraction.

That gas lift installations should be as permanent as possible is indicated from the foregoing considerations as regards surface equipment. It is the purpose of the present paper to show the development of means by which the pumping stage in a well's life can be taken by a system using compressed gas as the medium for lifting oil, and that such a system has a greater overall efficiency than pumping installations under a great many well conditions.

Our first consideration will be the main difficulties met with in pumping. To show the loads supported by the sucker rods the following example of a pumping well is taken:—

Depth: 4,400 ft.;
Tubing: $2\frac{1}{2}$ in.;
Rods: $\frac{3}{4}$ in.;
Pumping speed: 20 strokes per minute;
Length of stroke: 48 in.

For an estimation of the stresses which come into play the following factors should be taken into consideration:—

1. Dead load of rods;
2. Weight of oil supported on rods;
3. Force required to move the plunger in the working barrel;
4. Force necessary for the acceleration from rest to the maximum upward velocity attained during the up-stroke;
5. Force necessary to overcome the friction of the oil in the tubing.

Some of the above factors are difficult to estimate, but from a sucker rod load chart compiled from a series of Dynamometer tests in the field over a long period the following can be taken as a fair average for the above conditions :—

Dead load—14,000 lb. ;
Impulse load—18,000 lb. ;
Unit dead load—31,600 lb. per sq. in. ;
Unit impulse load—41,000 lb. per sq. in. ;
Elastic limit of rod material—60,000 lb. per sq. in. ;
Recommended maximum stress—22,000 lb. per sq. in.

From these figures it will be seen that instead of the maximum recommended stress of 22,000 lb. per sq. in. we have an impulse load of 41,000 lb. per sq. in., and that the elastic limit of the rod material —60,000 lb. per sq. in.—is too closely approached. Fatigue of the rod material is therefore bound to occur, and rod breaks will result. A crooked hole and a corrosive water condition will aggravate the above overloaded condition of the sucker rods.

The frequency of the pumping cycle is also an adverse factor, especially in relation to the fatigue of the sucker-rod material and wear of all moving parts. Twenty strokes a minute is 28,800 strokes a day, and during each stroke wear is occurring in the casing, tubing, sucker rods, and all pump parts. Other factors limiting the efficiency of the pump, especially on deep wells, are :—

1. Loss of stroke due to rod stretch ;
2. Buckling of the rods on the down stroke ;
3. Influence of temperature on the plunger and working barrel, if they are made of materials having different coefficients expansion ;
4. Influence of pressure on plunger and pump barrel. To illustrate : 4400 ft. of oil will exert a pressure of 1700 lb. per sq. in. The plunger will be on contraction and the working barrel in expansion ;
5. Plunger and valves operate against total fluid head in the tubing ;
6. Difficulty of determining the correct pumping speed, having in view the obtaining of the maximum production without pumping dry, and being as easy on equipment as possible.

The foregoing will indicate that although the pumping of oil wells is performed in many instances very efficiently, the system has in itself many inherent disadvantages, and that for the deeper wells pumping will not be found to be a satisfactory solution of the producing problem. A large number of present producing

wells in Rumania are, on account of depth, beyond the reach of efficient pumping. Future production will be mainly obtained from wells of similar and probably greater depths.

During the last few years there has been a great deal of development in the providing and improvement of systems to give the oil industry an alternative to pumping. The continued increase in the depth of oil wells has been the main incentive to development. However, results already obtained show that even for normal depths at which a pumping installation will work in a relatively satisfactory manner, there is a probability that systems pumping with gas will be more and more employed in the future.

The earliest form of lifting by this means has been practised for many years in various oil fields, and takes the form of a manually operated installation as shown in Fig. 1. Two strings of tubing

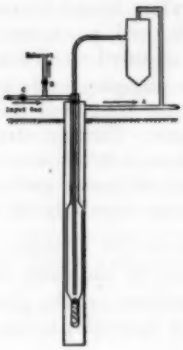

Fig. 1.

are run into the hole. The outer string is swedged out to form a filling chamber, and carries a standing valve and strainer at the bottom. The macaronie, or middle string, is run with its bottom end close to the standing valve. Formation gas exits from the casing into line A which is held at atmospheric pressure or under. The cycle of operations is divided into " on " and " off " times as follows :—

On Time.—Suppose chamber has filled with oil. Then valve B is closed and Valve C is opened. Input gas from compressors or other source enters the annular space between tubing and macaronie and oil in the chamber is forced into the macaronie and upwards into the separator.

Off Time.—Valve C is closed and valve B is opened. The pressure of gas in the chamber and annular space is exhausted to atmosphere. The standing valve is opened by the level of oil outside the chamber. As soon as the chamber is filled the cycle of operations is repeated.

There are many disadvantages in a system of this type. The input gas-oil ratio is necessarily high, and particularly so at deeper wells, on account of it being necessary to exhaust the pressure of gas in the chamber and annular space to atmosphere after each shot, and then again having to build up pressure from atmospheric pressure to the required pressure in the annular space in order to evacuate the chamber contents. The " on time " is of long duration, and as soon as it terminates a good time must elapse (while exhausting gas from the annular space, chamber, and macaronie to atmosphere) before the chamber is free to fill. Owing to the number of complete cycles which can be operated per hour being severely limited, oil outside the chamber may not be held at the desired level and reduced production would, in this case, be obtained. Having two valves to operate on the surface in order to complete each cycle is also a disadvantage.

There are conditions, however, under which such a system if operated automatically would have advantages. That is to say, for example, at fairly shallow small producing wells, and particularly so if there should be a supply of gas available from a high pressure separator. The cycle of operations can be operated automatically by the installation of a gastributor, and a magnetic two-way valve at each well. An eduction tube check valve should be installed at the bottom of the macaronie on a level with the top of the chamber in order to save gas and speed up the filling operation.

The Displacement Pump.

During the last year the system of gas pumping known as the displacement pump has been introduced into the Rumanian oil-fields. This system, using gas as the lifting force in place of sucker rods, is controlled automatically by a gastributor and magnetic valves in such a manner that the pressure exerted upon the formation is also due solely to the fluid head in the hole.

The gastributor is an electrical timing instrument operated by a synchronous type, 110 volt, single phase, 50 or 60 cycle electric motor, which drives the four timing wheels as a unit. Speed reduction is obtained by four sets of gears, three sets being enclosed and packed in grease. The other set and idler gear are exposed. By changing the two exposed gear wheels the speed of the timing wheels may be varied from approximately one to five hours per revolution. Each timing wheel controls a magnetic valve which,

when opened, allows gas to pass into the well. The timing wheels have trip fingers that ride up on the adjustable contact racks and actuate mercury switches with snap action. When a circuit is closed the corresponding magnetic valve opens and allows gas to pass into the well. The number of trip fingers and their relative positions around the wheel may be varied to give the correct time intervals between gas injections, and the duration of the gas injection period may be adjusted by a screw on the corresponding contact rack. Additional timing units can be added to this gastributor so that a maximum of 16 wells can be operated from it.

The magnetic valve is of single seated unbalanced poppet type, and is automatic in operation. When the gastributor closes the electric circuit to the valve, the electric magnet attached to it pulls in and opens the pilot valve, and permits gas from the compressor side of the magnetic valve to enter the piston chamber. The pressure of this gas forces the piston and stem down and opens the main valve. At the end of the injection period the gastributor opens the electric circuit and releases the magnet. This allows the pilot valve to close. A relief port then opens simultaneously, and the pressure in the piston chamber exhausts to the atmosphere which allows the main valve to be closed by a heavy spring.

The gastributor and magnetic valves were first used for intermittent gas lift with open end tubing in order to prolong the gas lift period. The displacement pump was a later development to be introduced into the well when the pumping stage has been reached.

The well installation of the displacement pump is run into the hole in the following sequence: the strainer, mushroom type standing valve, chamber, displacement pump valve shell, which carries the eduction tube and eduction tube check valve, and outer string of tubing is lowered to the desired depth and landed. The macaronie, or flow string, on the lower end of which is screwed the shoe of the displacement pump valve, is then run through the packing spider and lowered until the shoe of the displacement pump valve seats in the displacement pump valve shell. Input gas is delivered into the annular space between the tubing and macaronie through the magnetic valve shown on the by-pass.

Putting a Well on Production and Operation of the System.

Assuming that the design of the well installation has been decided upon, and the chamber and outside string of tubing have been run to the required depth and landed, the next step is to lower the displacement pump valve shoe and macaronie through the packing

spider. If the particular well builds up a high level when standing, it will be necessary to gas lift the well with the displacement pump valve shoe off seat, in stages if necessary, until the accumulated head of oil has been lowered to the chamber level. After this is done the shoe of the displacement pump valve is seated by lowering the macaronie and allowing sufficient weight to rest on the shoe in order to spread the three rings of lead packing on their corresponding seats in the displacement pump valve shell. On a 4000 ft. well it is found that half of the weight of the macaronie is sufficient for this purpose. A weight indicator installed at the well is useful in performing this operation. Everything is now in readiness to put the well on regular production. The input gas line to the well is opened and the first chamber full of oil is kicked out. It is at this point that the plunger of the displacement pump valve now comes into operation for the first time. As soon as the oil slug hits the trap, input gas is cut off and a suitable time interval is allowed for the second filling of the chamber. The operation is repeated manually until a time cycle is established. This time cycle is then adjusted on the gastributor which takes charge from then on.

The Cycle of Operations.

Off Time.—The magnetic valve at the derrick is closed and the standing valve at the bottom of the chamber opens and allows the chamber to fill. Pressure in the annular space between tubing and macaronie is held at the spring pressure in the displacement pump valve by the spring holding the plunger up against its top seat. Spring tensions of 150, 250 and 300 lb. are used in accordance with conditions. With the plunger in this position gas in the chamber is free to exhaust between the plunger and its lower seat through the port in the displacement pump valve shell, and into the casing which is held at atmospheric pressure or under.

On Time.—The magnetic valve opens as soon as the chamber has filled, and the high pressure gas available in the input gas lines up to each magnetic valve expands into the annular space and rapidly builds up pressure above the spring pressure of the displacement pump valve. This sudden expansion of gas, which is followed by the output of the compressors, slams the plunger down on to its bottom seat and holds it there. Gas then passes down the hollow stem of the plunger into the chamber, and forces the oil up the eduction tube, through the displacement pump valve, and into the macaronie. When the proper quantity of gas is behind the piston of oil the magnetic valve closes. Pressure in the annular space then decreases as gas expansion takes place

behind the slug of oil and a rapid sequence of events occur as follows :—

1. The plunger is forced by the spring on to its top seat, thereby retaining in the annular space a volume of high pressure gas available for the next shot ;
2. The eduction tube check valve closes and the expansion of gas under the slug of oil is forcing it to the surface ;
3. The exhaust port opens, exhausting gas from the chamber into the casing.

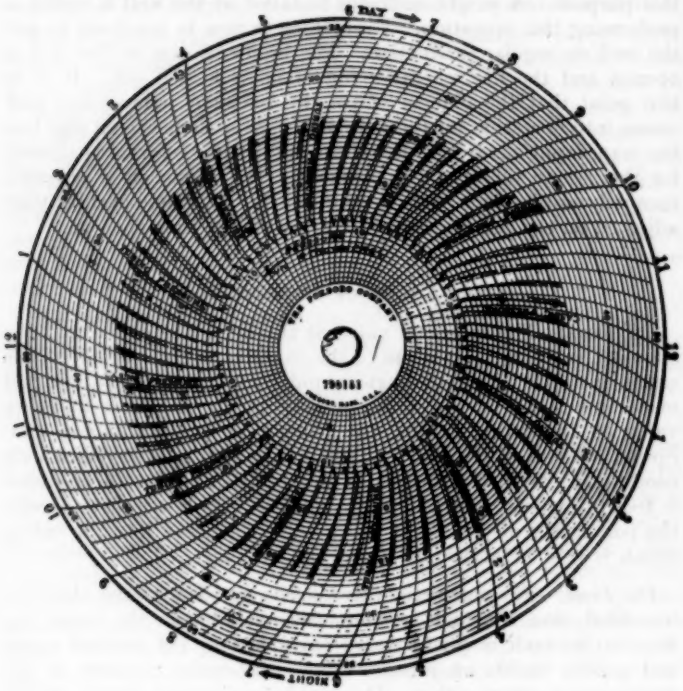

FIG. 2.

The design of the displacement pump valve is such that long periods of trouble free service can be obtained from it, providing clean input gas is used. It will be noted that the plunger, which has a total movement of 3/32 in., is only in contact with input gas and is removed by pulling the macaronie. The design of the plunger

is such that a chattering action is avoided, and it is held firmly either on its top or bottom seat.

The whole cycle of operations for a 24 hour period is shown on Figs. 2 and 3, on which is recorded pressure of gas in the annular space and output orifice meter readings respectively. These charts have been given by the kind permission of the Steaua Romana, and are from one of their wells in the Ceptura Field. In this particular case input gas is supplied from a gas well. The output orifice meter chart records the formation gas plus the input

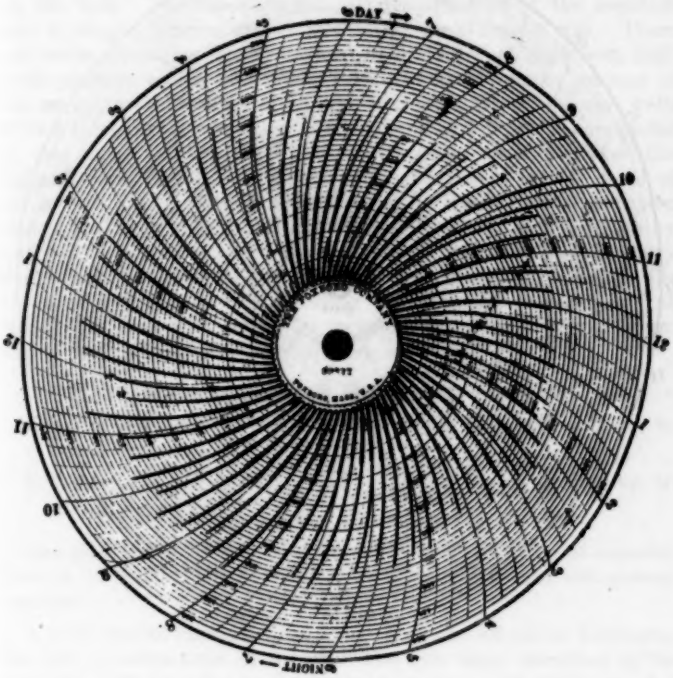

FIG. 3.

gas. The periodic extreme fluctuations of the differential reading are caused by the flow of gas following each shot. The thick black line which regularly occurs is caused by the plunger of the displacement pump valve coming on to its top seat and allowing gas to exhaust from the chamber to casing. Formation gas is

represented by the lowest differential reading. Fig. 4 is an hourly orifice meter chart of input gas. An hourly chart is used in preference to a 24 hour chart in order to show more clearly the fluctuations of differential pressure. It will be observed that for the three separate input gas cycles exactly similar readings are obtained.

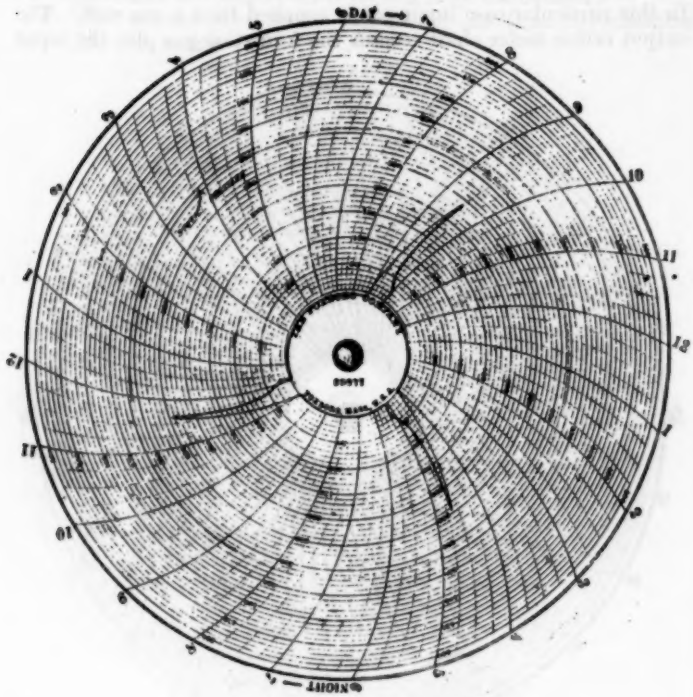

FIG. 4.

Therefore, the volume of gas measured for one cycle multiplied by the total number of cycles in 24 hours will give the volume of input gas used per day. Any defect in the mechanical parts of the system can be immediately detected at a glance at these charts. Or, in other words, there is a record on the surface of all underground operations.

Design of the Well Installation.

In considering a well for a displacement pump installation the following factors should be taken into consideration :—

Production Required and Depth to Run Chamber.—At a well free from sand and clay troubles, in order to obtain the maximum production it is necessary to produce with atmospheric pressure, or under, on the casing and to hold as small a level of oil as possible in the hole. For these conditions the chamber of the required size is run to bottom and it is emptied each time it fills. There are wells producing from a highly consolidated oil sand with high rock pressure which will produce practically the same amount of oil, no matter what level of oil is held in the hole. However, wells of this type are the exception in Rumania and will not be considered in this paper. Where sand and clay troubles are experienced the difficulty can usually be overcome by holding a certain level of oil in the hole. If the required level determined by estimation and experiment is held and not allowed to increase or decrease by any unreasonable amount, the conditions will be as satisfactory as obtainable for producing clean oil. At a well of this type the chamber is run with the standing valve to the lowest point at which it is considered advisable to empty the hole. Back pressure can be held on the casing if required.

Size of Installation.—There are two main sizes of installations :—

1. 1½ in. macaronie in 2½ in. A.P.I. tubing for producing up to about 2½ cars a day.
2. 2 in. macaronie in 3 in. A.P.I. tubing for producing up to about 7 cars a day.

The maximum production obtainable with each size of installation is, of course, dependent on well conditions and compressor capacity.

A great deal of experimentation has been carried out to determine the best combinations of tubing. The two main essentials to be complied with in order to obtain good results are that the annular space should be as small as possible, and that the I.D. of the macaronie should be of such size that the oil is brought to the surface in slug form at reasonable pressures. The importance of the small annular space is reflected in gas economy, and small interval of time to complete the cycle of operations. The action of the displacement pump valve in trapping a volume of high pressure gas in the annular space between tubing and macaronie

also greatly contributes to a low input gas/oil ratio being obtained. The following figures illustrate this point :—

Example taken : 4400 ft. of annular space between 1½ in. macaronie and 2½ in. tubing.

Spring.	Volume of gas in annular space.	Volume saved per day at well making 96 shots.
150 lb. ..	660 cu. ft. ..	63,360 cu. ft.
200 lb. ..	880 cu. ft. ..	94,480 cu. ft.
250 lb. ..	1100 cu. ft. ..	105,600 cu. ft.

If the above volumes in the annular space had been exhausted to atmosphere, as would be the case if the displacement pump valve should not be used, similar volumes would again have to be supplied by the compressor at each shot. There is also another important factor in that time is also saved. Each minute of "on time" saved gives a correspondingly longer filling time. With a compressor output of 500,000 cu. ft. per 24 hrs. the use of the displacement pump valve in the above example saves 1·9, 2·5 and 3·2, minutes of on time at each shot. It may be mentioned here that the input gas to gas/oil ratio under average conditions is 1000 to 1500 ft. per barrel of oil.

Capacity of Chamber.—The largest diameter chamber which can be safely run is decided upon. As regards length and capacity the following factors should be taken into consideration :—

1. Production to be lifted per day ;
2. Required number of shots or cycles to be operated per day and volume of liquid to be lifted per shot. 3—5 cycles per hour are generally employed ;
3. Head of oil formed in the macaronie at each shot. This head to be such that reasonable lifting pressures will be experienced, and of such length that appreciable gas slippage will not occur ;
4. Formation gas/oil ratio. When the volume of oil to be lifted per shot has been decided upon the quantity of gas entering the chamber with this oil must be considered, in order to determine the capacity of the chamber. At a well with a low gas/oil ratio, say, 1000 cu. ft./brl., it is probable that a filling efficiency of 80—90 per cent. can be obtained. That is to say the volume of oil received on the surface will be 80—90 per cent. of chamber capacity. With higher formation gas/oil ratios the chamber must be of correspondingly greater capacity.

Various Well Conditions in Relation to the System.

Wear on Equipment.—No matter under what well conditions the system is applied the wear of equipment down the hole is reduced to negligible proportions in comparison with a pumping well. The following example will illustrate this point :—

Pumping well : 20 strokes per min.	Strokes per day : 28,800 (300).	Wear : Tubing casing, sucker rods, all pump parts.
Displacement well : 4 shots/hour.	Shots per day : 96 (1).	Wear on : 1. Standing valve. 2. Eduction tube check valve. 3. Plunger of dis. pump valve.

The ratio of strokes to shots is 300 : 1, so that the number of cycles made during 300 days on displacement equals the number of strokes made by the pump in one day :—

1. Standing valve has large area of opening, and is held closed by the maximum lifting pressure, and not by the total fluid head in the tubing as in the case of a pumping well.
2. The eduction tube check valve is blown through with gas at each shot and closes against gas pressure.
3. Total movement of plunger is 3/32 in., and it is in contact with input gas only.

Depth and Crooked Holes.—There is no limitation in sight under this heading. In fact, the greater the depth the more advantage over pumping.

Sand.—Sand which enters the chamber with oil is carried upward and out of the well without coming in contact with the moving parts of the displacement pump valve. The top of the standing valve is blown free of any deposit by the rush of gas following each shot.

Water.—It cannot be said that emulsion will not be formed under all conditions, but owing to the liquid being lifted in slug form there is far less tendency to form emulsion than on gas lift. In certain cases where emulsion is formed it is found that oil and water settle out readily in the stock tanks.

Paraffin.—The general functioning of the system lends itself readily to the elimination of paraffin precipitation in the macaronie. The Steaua Romana have several installations in their Ceptura field, where paraffin conditions are particularly severe, which produce continuously for periods of about three months.

To prevent paraffin precipitation the main factor to guard against is the cooling of the oil on its way up the macaronie. It is preferable to take measures that will prevent this cooling and consequent paraffin precipitation rather than to deal with paraffin after it has once formed.

Where there is a bad paraffin condition the installation of an efficient steam heater for input gas is necessary. Then the various factors favourable to the elimination of paraffin precipitation are :—

1. Oil is produced in slug form at high velocity ;
2. Formation gas is produced separately through casing ;
3. Small volume of input gas used for lifting ;
4. Preheated input gas injected into the annular space raises the temperature of the macaronie to a high point before the slug passes.

One or More Displacement Pump Wells and Their Relation to the Compressor Plant.—In order to obtain the utmost economy from the compressors it is necessary that they should be continually under load. With one well arrangements will have to be made to blow off gas during the off times. Where a compressor of small output is used gas can be stored in a receiver and in the input gas line during the off times.

With two or more wells it is arranged that each well in sequence goes on " on time " and that at no period, except for gas storage, will all the magnetic valves be closed. It will be noticed that the installation of each magnetic valve at the well enables the input gas line to be used as a receiver.

Production Obtained with Displacement Pump as Against the Plunger Pump.—As regards back pressure on the formation, both displacement pump and the plunger pump are in the same category. That is to say, with both systems the rate of oil influx is dependent on the level of oil held in the hole. A pumping well, where the level is held well down, will not show an increase on a displacement pump well. However, on deep wells the various factors leading to lowered pump efficiency cause a level of oil to build up in the well which reduces the influx of oil. A displacement pump installation not subject to these adverse factors can reasonably be expected to show an increase.

Production on Displacement Pump or Plunger Pump after Gas Lift.—The introduction of a displacement pump or plunger pump should take place as soon as a well on gas lift shows signs that it is reaching the economic limit with this system. It is at this stage that the input gas/oil ratio begins to increase rapidly, and the back pressure held on the formation prevents the potential production of the well being obtained. As to what increase will be obtained depends on how much the back pressure on the formation is reduced and as to the sensitiveness of the sand to this decrease of back pressure. For instance, suppose a gas lift well with tubing to the top of the oil

sand is producing with 10 atms. pressure at the bottom of the tubing. The back pressure of this well on displacement or on the pump will be due only to the fluid head in the hole. It is, therefore, a simple matter to hold a small level of oil which will put a smaller back pressure on the sand than 10 atms. Measurement of pressure conditions in the fluid levels of a number of wells in Rumania having a fairly low formation gas/oil ratio has indicated that 1 atm. is equal to about 16 metres of oil level. Therefore, the 10 atms. in the above example would be equal to 160 metres of oil level.

The Use of High Pressure Separators.—During the recent months a number of companies have been making use of high pressure separators on flowing wells or gas wells for the supply of gas under pressure for various lease needs, and particularly for gas-lifting wells beyond the flowing stage. There are also instances of displacement pump installations operating on gas supplied from a high pressure separator instead of from compressors. It is probable that more attention in the future will be paid to obtaining the utmost use from gas delivered at the surface under pressure by the holding of the necessary well back pressure on a high pressure separator, or, if conditions require, partly on the Christmas tree and partly on the separator.

In fields where there is a supply of high pressure gas available for lifting oil out of wells beyond the gas lift stage there is the further advantage in employing a system using compressed gas for lifting oil in preference to a pump. In the event of gas not being available at sufficiently high pressure for direct use, it can be delivered to compressor intakes and boosted up.

DISCUSSION.

Mr. Hoegenboezen asked what kind of packing was used in the plunger of the displacement valve.

Mr. Chupp asked what effect the exhaust gas had on the pressure held on the casing.

Mr. Hodgson asked if displacement pumps were used for shallow wells, and if the system was economical for them.

Mr. G. Elias said that the whole question of how a well should be produced after the termination of its flowing life was of great importance to the production engineer, as he had to provide the necessary plant beforehand, and on the system adopted would possibly depend later the economic life of the well. The intermittent gas-lift system had now taken a definite place among the generally accepted production methods, especially in wells where the reduced rock pressure made straight gas lift uneconomical,

but where the gas lift installation remained available for future work at those wells. The system was nothing more or less than a highly developed intermittent gas lift, and the design made the control of gas variable over wide limits, but all the time the control was positive. Usual experience was that wells in the "Drader" sand were more difficult to produce than those in the "Meotic," owing to the thick bed of unconsolidated sand in the former. In any case, the usual practice employed at Meotic wells of producing them with straight gas lift from the end of their flowing life until the well was abandoned appeared to be satisfactory. In Drader wells, however, a point was reached when the reduction in rock pressure made straight gas lift no longer an economical proposition; they must then be pumped or produced by an intermittent gas lift system which did not put the pressure on the sand. Figure 5 shows the daily production of a Drader well during 1931. After the flowing life was finished, the well was pumped; it then became too dirty to pump, and it was bailed. The diagram showed how the production during bailing varied from day to day until the beginning of July. Since then the well had been on displacement, and produced very steadily and economically, at about a quarter of the bailing costs, excluding depreciation of the apparatus, which is costly. But it must be borne in mind that much experimental work had been done in perfecting the system. He would like to see the system tried on a Meotic third sand well producing one to two cars a day on gas lift from 1800 metres with a casing pressure of say 20 atmospheres.

Capt. J. E. Treacy asked if the system could be used with air where no gas was available.

Mr. V. C. S. Georgescu asked the author what he considered the lowest level at which oil could be produced economically by displacement.

Mr. Auer said he would like to mention a concrete case of a Drader well producing on the system, this well having produced steadily for six months up to date. The top of the producing sand was 940 metres, the bottom of the chamber, which was 39 metres long and of 4 in. diameter, being set at 888 metres. The well was running on 12-minute cycles, a 5 "on" and 7 "off," or about 120 shots per day, and the chamber filling efficiency was 63 per cent. The total liquid lifted was 16½ tons a day, about 8 per cent. being water. It was interesting to note that no emulsification took place. The formation gas-oil ratio was 50 cu. m./cu. m. and the input gas-oil ratio was 200 cu. m./cu. m. The oil contained 0·4 per cent. sand, but this had caused no difficulty either in choking valves or in showing signs of wear up to the present.

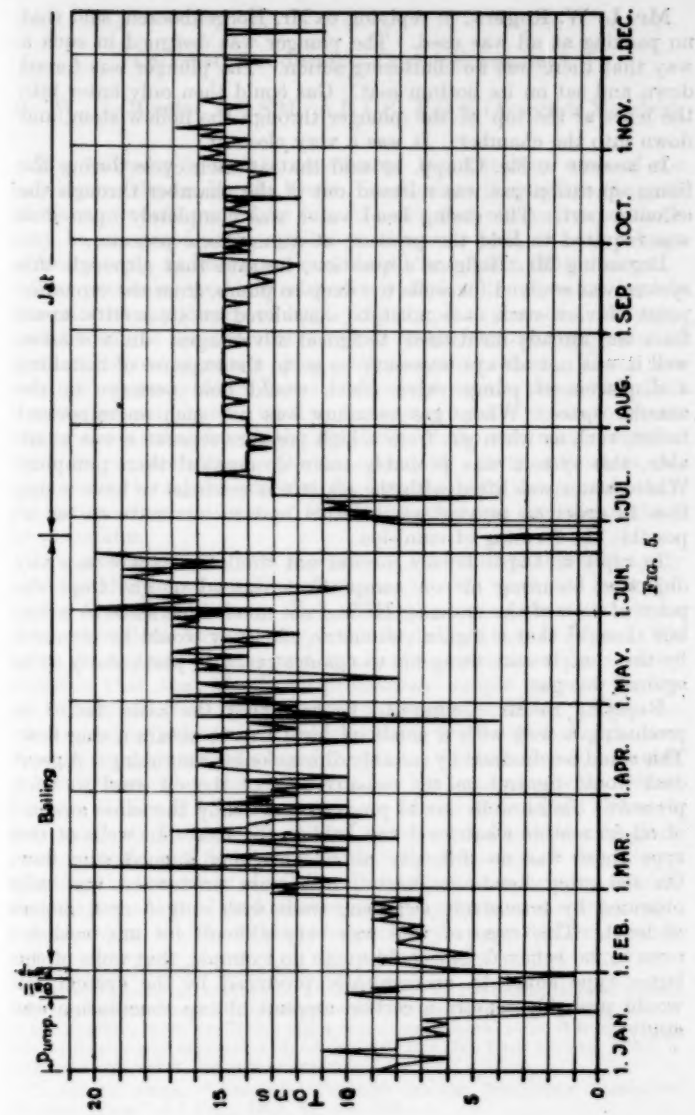
Dump
Bailing
Jet
1.JAN.
1.FEB.
1.MAR.
1.APR.
1.MAY.
1.JUN.
1.JUL.
1.AUG.
1.SEP.
1.OCT.
1.NOV.
1.DEC.
Tons
0
5
10
15
20

FIG. 5.

Mr. L. W. Rogers, in replying to Mr. Hoegenboezen, said that no packing at all was used. The plunger was designed in such a way that there was no chattering action. The plunger was forced down and sat on its bottom seat. Gas could then only enter into the holes at the top of the plunger through the hollow stem, and down into the chamber. It was a very close fit.

In answer to Mr. Chupp, he said that at each cycle during the filling operation gas was released out of the chamber through the exhaust port. The casing head valve was completely open if it was required to hold the pressure at atmospheric pressure.

Regarding Mr. Hodgson's question, he said that although this system was evolved for wells too deep to pump, from the economic point of view each case must be considered on its merits, apart from the already-mentioned technical advantages. In a shallow well it was not always necessary to go to the expense of installing a displacement pump valve which would hold pressure in the annular space. Where gas economy was not such an important factor, such as when gas from a high-pressure separator was available, this system was probably more economical than pumping. Where water was lifted with the oil, it was essential to have a slug flow in order to prevent atomization and to eliminate as far as possible the forming of emulsion.

In reply to Capt. Treacy, he did not think that there was any objection to using air on compressors instead of gas from the point of view of the system. He had not much experience to go on, but thought that a higher volumetric efficiency would be obtained by the compressors using air as against gas, and particularly so as against wet gas.

Replying to Mr. Georgescu, he said that the main factor in producing a well with a small oil level was to obtain a slug flow. This could be obtained by suitably dimensioning the tubing. A great deal would depend on the sensitiveness of the oil sand to back pressure. Some wells would produce practically the same amount of oil no matter what level was held in the hole. In wells of this type there was no difficulty about obtaining a good slug flow. On the other hand, in Poland, maximum production was only obtained by intensively swabbing wells with only 5 or 6 metres of level. This type of well was very difficult for any system; even so, he believed, but could quote no example, that wells of this latter type could be economically produced by the system, but would probably require a certain amount of experimentation and study.

Oil-Well Production-Curve Formulæ.*

By W. G. Weeks, A.R.S.M., A.R.C.S., F.G.S. (Associate Member).

The following is mainly an attempt to controvert some of the conclusions drawn by Mr. Owen,[1] and, since it employs the performance records quoted by him in order that alternative methods may be compared when applied to the same well, it is to a large extent a reply to his paper, and should be read in that context.

The particular problem which it is wished to examine here is the relative expediency of employing simple exponential or hyperbolic† formulæ for the curves which result from plotting rates of production or aggregate productions against time. There are formulæ of many other forms that would satisfy the curves, but they are less simple; and, until we have some *a priori* reason to favour any of these other forms, the simplicity of the two named entitles them to our preference. Of these two, Mr. Owen advocates the exponential form; he excludes the hyperbolic on the grounds that, if a natural time scale is used, it fails to satisfy two conditions which he postulates.

It is true that if we were in search of a formula that would apply to the production of a well at all stages of its life we should be bound by Mr. Owen's conditions. But, although such a formula would be most convenient, have we any reason to believe that it exists? We have, in applied physics and mechanics—sciences of far greater precision than that of oil-well production—ample warrant for the use of formulæ that are applicable only between limits. Thus the law connecting pressure and volume during the isothermal expansion of a gas is constantly employed in spite of the fact that it is known to break down when the gas approaches the liquefying point. Also, the laws of flow of a fluid in a pipe are known and utilised although they suddenly alter at the critical velocity at which steady gives place to turbulent flow. Considering the intricacy of the factors affecting the behaviour of an oil well, it would seem far more tenable that the same laws of performance do not apply from start to finish; and, therefore, that we ought to be content if we can find expressions

* Paper received November 28th, 1931.

† Strictly speaking, this term is, I believe, used by mathematicians to denote only expressions in which the exponent of the independent variable is −1. In the absence, however, of any other convenient general term, it is employed here to denote any expression of, or derived from, the form $y=ax^n$, where n may have any value, positive or negative.

[1] Launcelot Owen, "Empirical Formulæ for the Production Curves of Oil from Wells," *J.I.P.T.*, 1931, **17**, 500–505.

which accurately reproduce the well's behaviour over limited periods, without requiring them to apply equally well to the often very irregular early stages, and to the infinite period that would theoretically elapse before the well ceased to produce.

As a matter of fact, the hyperbolic form is not excluded by Mr. Owen's second condition. Nor is it by the first unless we insist on a "natural time scale," by which I understand Mr. Owen to mean that time must be reckoned from the moment when the well is first produced. But this requirement seems again to arise from the assumption that a single law will apply throughout. If there is more than one law, then to insist on the use of a natural time scale is tantamount to assuming that the same quantity of oil would have been produced in the same time by two different laws, whereas it is obvious that the production up to the time when the law changed would almost certainly have been reached under the later law, had it been operative throughout, in a different time to that in which it was reached under the earlier one. Moreover, there seems to be little, if anything, to be gained by adhering to a natural time scale. At first sight it appears that it would simplify calculation if we could always reckon time from the date at which the well first started to produce. But there are few wells in which production is not interrupted at some time after the first flow, often during the first few weeks; and, as the duration of these interruptions bears no relation to the rate of production, it is necessary to allow for them when seeking a relation between production and time. The reckoning of the time is, therefore, rarely quite straightforward, so that the very slight extra complication introduced by the addition or subtraction of a constant, which, as will be shown later, is the only adjustment necessary to obtain a time scale to which the hyperbolic form is applicable, is hardly worth considering.

Mr. Owen's arguments against hyperbolic formulæ, therefore, hardly appear sufficient to justify our rejecting them out of hand. But this does not necessarily imply that they are better than exponential. A general and decisive answer could only be obtained deductively; but, in the present state of our knowledge, hardly seems likely to be forthcoming. When it is, it may quite possibly condemn both forms. But, until it is, the only sound criterion by which we can judge between alternative formulæ is their ability to yield calculated results in close agreement with our observations. The form we decide to adopt in any given case, therefore, will depend on experiment. But, although, proceeding thus inductively, we can never obtain a logically perfect proof that one or the other is universally the better, if we find, as we pursue our examination of well records, that one form consistently gives better results than the other, we shall soon be justified in claiming that there is a strong

presumption that one form is the better for all wells. Mr. Owen tells us that he has been successful with exponential formulæ : the writer, on the other hand, has never used exponentials, but has obtained good results with hyperbolic expressions in all cases he has examined. It will be of interest, therefore, to try the hyperbolic method on a well with which Mr. Owen claims to have been successful with the exponential, and compare the results.

Mr. Owen's data, given on page 502, are rather scanty, but seem to be sufficient for our purpose. For convenience they are tabulated as follows :—

Time (weeks) t.		Rate of production (brls. per week) P_t.
Zero	..	7000
4	..	5425
11	..	4200
30	..	1575
38	..	1260
65	..	630

From these figures he deduces the following expression :—

$$P_t = P_0 \times 1{\cdot}036^{-t}$$

where P_t represents the rate of production in barrels per week at time t in weeks after the well's first production ; and P_0, the rate of production in barrels per week at zero time (initial production).

Using this formula, the rates for the different times at which we have observations have been calculated and the results are given in the following table :—

t.		P_t observed.		P_t calculated. $P_0 = 7000$.		Error %.
4	..	5425	..	6077	..	12·0
11	..	4200	..	4744	..	13·0
30	..	1575	..	2422	..	53·8
38	..	1260	..	1826	..	44·9
65	..	630	..	703	..	11·6

It will be observed that the errors are considerable and all in the same sense.

In the calculations below, the cited observations, as they stand, were not employed because, when they are graphed, they are not found to lie on a smooth curve. Their departures from a smooth curve may, however, be explained by errors of observation, as Mr. Owen suggests, and we can thus obtain closer approximations to the true values by drawing an average curve. Since, however, the later results will be compared with these amended values, and not only with the original observations, it may be felt that we ought to treat the values calculated from Mr. Owen's formula in the same way. The errors were, therefore, recalculated, using

the amended values, but omitting the observation at the end of four weeks for which no trustworthy graph-value was obtainable. The result does not materially diminish the error.

A formula giving such errors as the above can hardly be considered satisfactory, but need not be taken to condemn the exponential form, even for this particular well, because it may not be the best; and it remains to be shown that a hyperbolic formula will give better results than the best exponential. Since there are only two constants in the exponential form, they can be determined by the use of two pairs of observed values which the resulting formula is then bound to satisfy exactly. If its form is suitable it will also satisfy all other points. It should be a matter of comparative indifference which two pairs are taken, but to reduce observational errors we select the two that are farthest apart, and these should give the best formula. In order to decide whether the hyperbolic form is better, we must deduce formulae of both forms from the same set of observations, and compare the closeness with which values for intermediate points calculated from them agree with the observed values. Before doing so, the observations will be retabulated with the more probable values from the graph, and using days and barrels per day as more convenient units. We obtain thus for our fundamental data:—

Time: days. t.		Rate of production: bls. per day. r.
28	..	?—
77	..	525
210	..	230
266	..	176
455	..	90

The general exponential formula is:—

$$r=P_0K^t$$

where I have substituted r for P_t, Mr. Owen's symbol for rate of production. r is now in barrels per day; P_0, the initial rate, in the same units; and t, the time, in days since the well started to produce.

Substituting the values (r=525, t=77) and (r=90, t=455) in this equation, we solve for the constants P and K, and obtain as the particular formula for this well:—

$$r=751.9\times0.995345^t$$

from which, by substituting the intermediate values of t, we can calculate the intermediate values of r. If the formula is satisfactory they should approximate closely to be observed values. These calculated values will be given later when we come to compare the results of the two methods.

The general hyperbolic formula is:—

$$r = aT^n$$

where r has the same meaning as before, a and n are constants, and T is equal to $t \pm y$, where t is time in producing days since the well started to produce, and y is a constant which has to be introduced because, while the relation between rate and natural time is not hyperbolic, that between rate and natural time plus or minus a constant appears to be so, or very nearly. We may, in effect, consider that t contains a concealed constant, $\pm y$, by eliminating which the relation between rate and the variable part of the time term is enabled to show its hyperbolic nature.

The method of obtaining the value of y will be dealt with later. Assuming that we have it, we substitute the same values of r and t as for the exponential, and solve for the constants, which gives us for the particular formula:—

$$r = \frac{10{,}256{,}000}{(t+153.4)^{1.8162}}$$

the time term going below because n is found to be negative. From this, as before, we obtain the intermediate values of r by substituting the intermediate values of t.

Both methods will, of course, give correct values of r at t=77 and t=455 because these were used in determining the constants. The test is their agreement with the observed values at other points. In the following table are given the intermediate values of r calculated by both methods, together with the graph values, and the observed ones where we have them, for the same times. In addition to those at the two observed points a number of other intermediate values have been calculated because, in determining y, it was necessary to use an intermediate value of r which happened to fall between the two observed points, so that the close agreement at those points between the hyperbolic and observed values might have been due rather to their proximity to this value than to the correctness of the curve.

t	Values of r. Observed.	Graph.	Exponential.	Hyperbolic.
100	—	443	472	442
150	—	322	373	319
210	225	230	282	229
266	180	176	217	177
300	—	150	185	154
350	—	121	147	127
400	—	103	116	107

It will be seen at once that the exponential curve departs widely from the graph. On the other hand, the hyperbolic agrees

with it so closely that its discrepancies are little greater than the limits of possible error in drawing and reading the graph. For this particular well then, between the given limits, a hyperbolic formula has been shown to be superior to an exponential.

A convenient method of testing the applicability of the exponential form to the production-curves of any well is to plot the daily productions (i.e., the rate in barrels per day) on semi-logarithmic paper, with production along the logarithmic and time along the natural axis. If an exponential form is suitable, the resulting graph will be a straight line. The writer has never yet obtained a straight-line graph by this method. The use of semi-logarithmic paper is very convenient, apart from its value as a test, because it keeps the graph within practicable limits of size without unduly reducing the scale for the lower values of production, and makes the fluctuations at different periods of the well's life more easily comparable.

In his paper, Mr. Owen tells us that by the use of his formula he was able to forecast correctly that the rate of production of his selected well would fall to 10 barrels per day after 130 weeks, and that, by this time, its total production would be about 196,000 barrels. By the hyperbolic formula deduced above, the rate at 130 weeks (910 days) would have been between 32 and 33 barrels per day. We are faced, therefore, by the curious fact that a formula, which in the past gave errors of over 50 per cent., was better for prediction than one which, as we have seen, followed the past curve almost exactly.

There seems to be no escape from the conclusion that the correctness of Mr. Owen's forecasts was the result of a fortunate accident. In using any formula based on past results to foretell the future, we make the inevitable assumption that the past law will continue to prevail until the time of our prediction. But if our law is inaccurate over the period during which it can be checked, what possible grounds can we have for relying on its accuracy in the future? In this case, also, there are reasons for thinking that some change of law must have taken place between the 65th and 130th weeks. At the 65th week, the well was apparently flowing at the rate of 90 barrels per day through unchoked 2-in. tubing. We are not told what happened between the 65th and 130th weeks, but surely some alteration must have been made, since it would be a very exceptional well that would continue to flow under these conditions until its rate had fallen to 10 barrels per day. But an alteration can hardly have been made without some effect on the production law, in which case neither of our formulæ would any longer have been applicable.

The utility of any of these formulæ in long-period forecasting is in fact very doubtful. Reference has already been made to the general grounds upon which we should expect changes of law to occur, and the writer has never analysed the records of a well without finding evidence of them. The changes are, of course, often due to alterations in production methods, but there are numerous instances for which no such explanation can be offered, and whose causes appear rather to be in some way inherent in the well's natural conditions. Moreover, it can practically be proved that they must be anticipated because, not infrequently, during its early life, a well will follow laws which, if they persisted, would give colossal productions which we know for certain it could never reach no matter how skilfully it was produced. The writer had occasion recently to analyse the records of a well which had been flowing for over a year and had followed perfectly for many months a hyperbolic decline. Had the same decline law persisted, it would still have been flowing 150 barrels per day when it had yielded 1,000,000 barrels, and would have ended by giving several millions. While we do not yet know what that particular well will produce, it is most unlikely to exceed half-a-million barrels, and may fall far short of that. For that well, therefore, we should have been bound to anticipate changes of law no matter how it were treated, and since we know neither when they will occur nor what the future laws will be, any attempt to forecast its ultimate recovery from its past performance would obviously have been futile. The principal value of these formulæ is, in the writer's opinion, to allow us to make accurate, short-period forecasts in order that we may compare a well's performance after some deliberate alteration with what it might reasonably have been expected to be had no alteration been made. Even then, we ought always to bear in mind that our period of forecast may happen to coincide with a time of inevitable change. A minor use of the formulæ is to give us, for what they are worth, maximum values of a well's possible production, since, assuming efficient production methods, the changes of law appear always to be for the worse.

In the last paragraphs it has been implied that our formulæ enable us to calculate aggregate productions as well as rates. The expressions for this are, of course, obtained by integrating the rate equations. The integral of the hyperbolic formula for Mr. Owen's well is :—

$$p = C - \frac{12{,}565{,}000}{(t+153.4)^{0.8162}}$$

where p is the aggregate production in barrels at time t in producing days, and C is a constant, to determine which we put p and t equal

to zero and solve, getting C=206,500. Since the second term disappears when t becomes infinite, C represents the total theoretical production of the well. It will be noticed that it is a few thousand barrels higher than the 198,000 barrels which Mr. Owen gives for the total theoretical supported by the actual performance of the well. The difference between the total theoretical by the hyperbolic method and the actual is due in part to the commercial impracticability of extracting every drop of oil, but may also be the effect of a change of law.

In the above example, the hyperbolic production-time formula was perforce determined from the records of rate of production, because they were the only ones available. In practice, the writer has been in the habit of determining the production/time formula first, and of deriving the rate/time expression from it by differentiation. Values for the rate are then calculated and plotted on the daily production graph. This affords a check, and as a rule they agree very well.

Both the production/time formula determined in this way and the rate-time formula derived from it plot as straight lines on logarithmic paper, and by combining the two on the same sheet a useful diagram is obtained from which the value of both production and rate at any future time can be seen at a glance. The diagram thus serves the same purpose as the popular "rate/cumulative" curve, but is superior to it in giving time as well. But both suffer from the same defect; they assume that there will be no change of law.

It is possible, however, that the approach by the rate/time formula is the better. When determining the production/time formula first, its form is assumed to be $p=a(t+y)^n$. But if we obtain the production/time formula via the rate/time formula, this form only appears when the exponent n in the rate/time formula is less than 1. If it is greater than 1, we get the form which has already been derived for Mr. Owen's well. The two are fundamentally different in that the former has no integration constant and tends to infinity, while the latter is asymptotic to its integration constant. Also, with the latter, we do not obtain a straight-line graph on logarithmic paper by plotting production and time: to get a straight line we must now plot time against theoretical *production remaining*, which is not, however, without its advantages. The difference in form of the two production formulæ may be due to the wells being of different types, or it may arise from the direction of approach. This can only be determined by trial with actual records, of which, unfortunately, the writer has none available at the moment. Should the former supposition prove correct, the form of the equation suggests several

interesting lines of investigation, which cannot, however, be discussed here. It may be noted that the approach through rate/time will have to cope with the greater difficulty of obtaining good values for substitution from the rate than from the production records on account of the much more violent proportional fluctuations of the former.

In a recent conversation with an employee of one of the big oil companies the writer was surprised to learn that, although they were using the same general hyperbolic method as that described above, they were obtaining the y constant by a tedious method of trial and error. It may, therefore, be of interest to show how it can be determined by a quite simple calculation.

Assume that we have the aggregate production for a well for any time in producing days after it was brought in, and that it is required to find y in the formula $p=a\,(t+y)^n$ as above. Let $T=(t+y)$. Then log T is a straight-line function of log p, so that equal increments of log p must be accompanied by equal increments of log T. Take two values of p, say p_a and p_z, at the beginning and end of some portion of the production/time records during which no change of law has occurred, and determine a value p_m such that log p_m is the mean between the logarithms of the two extremes. In other words, find the geometric mean between p_a and p_z. From the records or the graph determine the value of t corresponding to p_m. Then, since the increment of log T between its values at the times corresponding to p_a and p_m, say t_a and t_m, is to be equal to the increment between its values at the times corresponding to p_m and p_z, say t_m and t_z, y must have such a value that,

$$\log (t_m+y)-\log (t_a+y)=\log (t_z+y)-\log (t_m+y)$$

whence, by a simple solution,

$$y=\frac{t_m^2-t_at_z}{t_a+t_z-2t_m}$$

A similar method will give y in the rate/time formula if we prefer to determine that first.

The above has been referred to Mr. Launcelot Owen, who writes as follows :—

As there appears to be some misapprehension as to the object and claims of my note on "Empirical Formulæ," printed in the Journal for August, 1931, I would like to add the following comments.

My note was written as the result of personal experience in applying various types of curves to production data of the nowadays rather rare cases of wells which had been allowed to flow over long periods without artificial aid or interference, and I attempted

to show that the unqualified rejection of the possibilities of the exponential form for the correlation of production data, in favour of the hyperbolic and other forms, was not justified.

I did not claim that any exponential expression could be made to tally accurately with the usually scattered points one obtains by plotting production figures. The inherent lack of precision in the measurement of oil production, under normal field conditions, would make any such agreement extremely improbable, whatever the type of curve employed.

What I did claim, however, is that—using a straightforward time scale—the exponential form is capable of giving values in *general agreement* with the production data and, given reasonably settled conditions, that it may be usefully employed for extrapolation.

My objection to the hyperbolic form (using the term in a wide sense) is that there does not appear to me to be any sound theoretical reason for its employment and, in order that it may fit the case at all, it has to suffer arbitrary abridgment. It is obvious that almost any plane curve can be made to fit a series of values, approximately, if it is considered allowable to behead and/or curtail the curve at such points as may happen to suit the particular case under consideration. The analogies, cited by Mr. Weeks, as justifying the employment of beheaded and curtailed curves, are surely not applicable to a naturally flowing well where the conditions, although admittedly complicated, are hardly likely to involve drastic changes in physical state or velocity.

"t" in what I called my "natural time scale" indicates the number of units of time during which the well has been actually producing. Shut-down periods are not included. It may be noted here, however, that, after a lengthy shut-down, the conditions within the reservoir may be so changed as to require a new value for P_t and for C. As pointed out in my note, it is only in the absence of geological catastrophies (again using a term in a wide sense) that one equation covers the life of a well.

With reference to the well quoted, the shut-down periods happened to be small, compared to the unit of time employed, and were fairly evenly distributed. For the sake of simplicity, therefore, they were ignored and the time scale, in that particular case, is also a date scale.

With reference to the initial production figure of 7000 barrels, as stated on p. 502 of my note, I consider this to be in excess of the true value. The adoption of a figure slightly below 7000 would, of course, reduce the percentage errors calculated by Mr. Weeks, but, as might legitimately be expected, certain points would still lie at some distance from the theoretical curve. The particular well

quoted was chosen, by the way, because I happened to have the figures available in a report dealing with quite another matter and not because it was particularly favourable to exponential treatment.

I agree, of course, that a selected hyperbolic curve may often give quite good accordance with production data, but, to achieve this accordance, arbitrary beheading and/or an arbitrary time scale are necessary and this, in my opinion, is a great disadvantage if one is seeking some expression which is capable of general application.

For short-dated extrapolation of production data, my own experience is that straight-line projection gives, in the majority of cases, results as accurate as the more complicated methods.

Where general application is not the goal, data from individual wells can be correlated (and integrated) more or less satisfactorily by a very varied collection of expressions. Those interested in mathematical gymnastics may find amusement in the application of a modified exponential of the form :—

$$P_t = P_0 C^{-t} \left(1 - \frac{\sin t\theta}{t}\right)$$

In such operations, however, I think that we might well recall an *obiter dictum* of the late Professor John Perry :—

" When joining up any series of data by a curve, remember that, in the formula expressing the curve, a most important factor is gumption."

REVIEW.

TUNNARD'S TANKER TABLES. B. Tunnard. Second edition. Pp. 78. Glasgow: Brown, Son & Ferguson, Ltd. 1932. 7s. 6d. net, postage 4d.

The first edition of these tables was published in 1928, and the second edition has been extended to cover the metric system. The book opens with some practical notes on problems relating to the measurement of oil, following which is a series of conversion factors for volume to weight and vice versa. These are stated to be based on the latest determinations of the International Bureau of Weights and Measures. Factors are given for both 60° F. and 62° F., with the stated object of overcoming the difficulty occasioned by the use of these two temperatures in metrology.

While it is obvious that a given volume will have different weights at varying temperatures, it is difficult to see why different conversion factors are given for the comparison of volumes. For instance, it is stated that 1 gallon at 60° F. is equal to 0·160543 cu. ft. of water at 60° F., while 1 gallon at 62° F. is equal to 0·160544 cu. ft. at 62° F.

The main part of the book consists of tables giving cubic feet, Imperial and American gallons, barrels and litres per ton of 2204 lbs. and per metric tonne of 2204·6223 lbs., and the weight in pounds and kilogrammes for each of the four volumetric units, at various specific gravities from 0·650 to 1·0. Densities by the A.P.I. scale are also included, and all the calculations are based on the conversion factors given for a temperature of 62° F.

A few remarks on the handling of oil cargoes concludes the work. The book is well printed, and should be of value to those who have to deal in any way with petroleum cargoes. GEORGE SELL.

BOOKS RECEIVED.

MODERN COAL CLEANING PLANT. Sydney H. North. Pp. iv.+159. London: E. & F. Spon, Ltd. 1932. 5s. net, postage 6d.

Though not so intended, this book is of considerable interest to oilfield engineers and drilling staffs in that it gives a very full description of methods and machinery for separating particles of suspended matter from fluids.

The problem of separating shale from fine coal is different in some aspects from the oilfield problem of separating shale from drilling mud, but some of the machinery used by the coal-mining engineer has already been adapted by the oilfield engineer to the new purpose, and more or different types might possibly be used by him with advantage. A study of this book will give the oilfield engineer a very clear insight into all available types of machinery and methods, all of which are fully and comprehensively dealt with.